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The Effect of Vanadia Surface Treatment on the Corrosion Inhibition Characteristics of an Advanced Magnesium Elektron 21 alloy in Chloride Media

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An advanced magnesium Elektron 21 alloy has recently been developed as a possible alternative to aluminum and steel based alloys for transportation industries. The newly developed Elektron 21 alloy characterises with its high corrosion resistance in chloride solution, excellent mechanical properties and light weight. Our group has recently developed high performance vanadia protective coatings of self-healing functionality that have been used to improve the surface resistance of different magnesium and aluminum alloys. This paper addresses an attempt to make functionality of the vanadia coatings we designed to improve the corrosion resistance of the newly developed Elektron 21 alloy in corrosive environment. The corrosion inhibition characteristics of Elektron 21 alloy were studied at different vanadia solution concentrations namely 10, 30 and 50 g/l at the neutral vanadia solution pH. Electrochemical impedance spectroscopy was used to evaluate the electrochemical behavior in 3.5% NaCl. Results confirmed the acceptable pitting corrosion resistance of Elektron 21 alloy. However, crevice and general corrosion were observed. Unlike all previous Mg and Al alloys we studied, vanadia coatings has an adverse effect on the corrosion protection of Elektron 21 alloy due to formation of inhomogeneous coating of mixed oxides of neodymium, gadolinium, zirconium in addition to vanadia as identified by SEM-EDS.

Keywords: Advanced materials, protective coatings, Elektron 21 alloy, surface treatment, transportation materials.

1. INTRODUCTION

Magnesium possesses the lowest density among all metallic constructional materials, high specific strength as a substrate, and good castability and weldability characteristics. Unfortunately, magnesium has high chemical affinity and reacts with atmospheric oxygen and water resulting in the formation of porous oxide carbonate film on the surface [1-6] which does not offer protection. The metal corrodes even in moist air and in distilled water. The situation is even more complex for magnesium alloys.

Chromium (VI) compounds were widely used for producing conversion coatings [2-9] to protect magnesium, aluminum and steels alloys. In spite of its toxicity, chromium (VI) has remained an essential ingredient in the metal finishing industry for corrosion control. But combine the economic impact of corrosion damage, the environmental and health problems cause by chromium (VI), and the increasing regulatory restrictions, scientists have a huge incentive to develop a new generation of protective coating systems.

A newly developed vanadia based protective coating was successfully designed by our group to improve the corrosion resistance of many magnesium and aluminum alloys such as Mg AZ31, Mg AZ91D, Mg ZE41, Mg AZ31 HP-O, AV31A T6 alloys and AA2024 T3 [10-17].

Recently, an advanced magnesium based alloy called Elektron 21 has been developed as a possible alternative to aluminum and steel based alloys for transportation industries. According to the manufacturer [18], the newly developed Elektron 21 alloy characterises with its high corrosion resistance in chloride solution, excellent mechanical properties and light weight. The alloy was developed for motorsport and aerospace applications and designed to provide superior mechanical properties and improved corrosion resistance together with good castability. As listed in its specifications [18], Elektron 21 alloy has achieved Aerospace Material Specification AMS 4429 and is the first magnesium alloy ever to achieve full MMPDS (MIL-HNDBK-V) design handbook entry, including statistical A & B values and elevated temperature information. It was stated also that the alloy showed superior corrosion resistance (0.13-0.37 mg/cm^2/day), 10-30 MPY as measured by salt spray test (ASTM B117) [18]

The objective of this paper is to study the corrosion behaviour of specimens of Elektron 21 alloy after one week of immersion in 3.5% NaCl solution open to air at room temperature. The effect of vanadia coatings (that were previously designed and provided superior corrosion resistance and self-healing functionality to several Mg and Al alloys [10-17]) will be investigated for Elektron 21 alloy. The electrochemical behavior and resistance to localized corrosion were studied by means of EIS technique. Surface examination was performed by optical microscopy, SEM-EDS and visual inspection.

2. EXPERIMENTAL

2.1. Materials and Surface preparation

Specimens of Elektron 21 alloy provided by Magnesium Elektron, UK, in the form 30 x 60 x 3mm were cut from a sand cast plate 100 x 200 x 25mm, and abraded to 800 # finish with SiC grit papers, degreased in acetone, washed with distilled water, and dried in dry air. The alloy chemical composition is Zinc 0.2-0.5%, Neodymium 2.6-3.1%, Gadolinium 1.0-1.7%, Zirconium saturated and Magnesium balance.

As provided by the manufacturer, Elektron 21 is a new high strength fully heat treatable magnesium based casting alloy for use at temperature up to 200 C. The new alloy has been developed to offer improved properties and superior corrosion resistance whilst maintaining the processing advantages of the Mg-Zn-Rare Earth alloys [18].

2.2. Solutions and surface treatment:

The vanadia coatings are deposited from aqueous solutions containing sodium vanadate using a very simple spontaneous free immersion processing technology that is very similar to that currently used for the toxic chromate system. A thin layer of vanadium oxide conversion coatings is deposited on the magnesium alloy surface by a chemically driven deposition process. Typically, uniformly distributed compact coatings of thickness about ~ 1.5-2.5 μm were deposited.

Solutions used in this work were prepared using sodium vanadate salt with different vanadia solution concentrations. The magnesium Elektron 21 alloy substrates were treated directly by simple free immersion in vanadia solutions of different concentrations namely 10, 30 and 50 g/l.

2.3. Testing:

Electrochemical Impedance Spectroscopy (EIS) technique was used to evaluate the electrochemical behavior of the uncoated (as-polished) and coated magnesium samples in 3.5% NaCl solution open to air and at room temperature for up to one week.

A three-electrode set-up was used with impedance spectra being recorded at the corrosion potential E_{corr}. A saturated calomel electrode (SCE) was used as the reference electrode. It was coupled capacitively to a Platinum wire to reduce the phase shift at high frequencies.

EIS was performed between 0.01 Hz and 65 kHz frequency range using electrochemical analyzer instrument: CompactStat Ivium Soft 1.805 Release, IVIUM Technologies Netherlands. The amplitude of the sinusoidal voltage signal was 10mV. The exposed surface area was 4 cm^2. All curves were normalized to one cm^2.

2.4. Surface characterization:

SEM-EDS were used to examine the surface morphology of the coated samples before and after corrosion in 3.5% NaCl solution. SEM images of the corroded samples were obtained using a Gemini LEO 1550, 3kV operating voltage, Zeiss, Germany. Some SEM images were obtained by an Environmental Scanning Electron Microscopy, ESEM, FEI Quanta 600F, USA.

Microprobe analysis was performed using DSM 940, Thungsten Kathod, Zeiss, Germany, coupled EDX ISIS, SiLi-detector, energy resolution 133 eV, Oxford. Each analysis was preformed three times at different spots using screen analysis at very high magnification covering the all size of the spot.

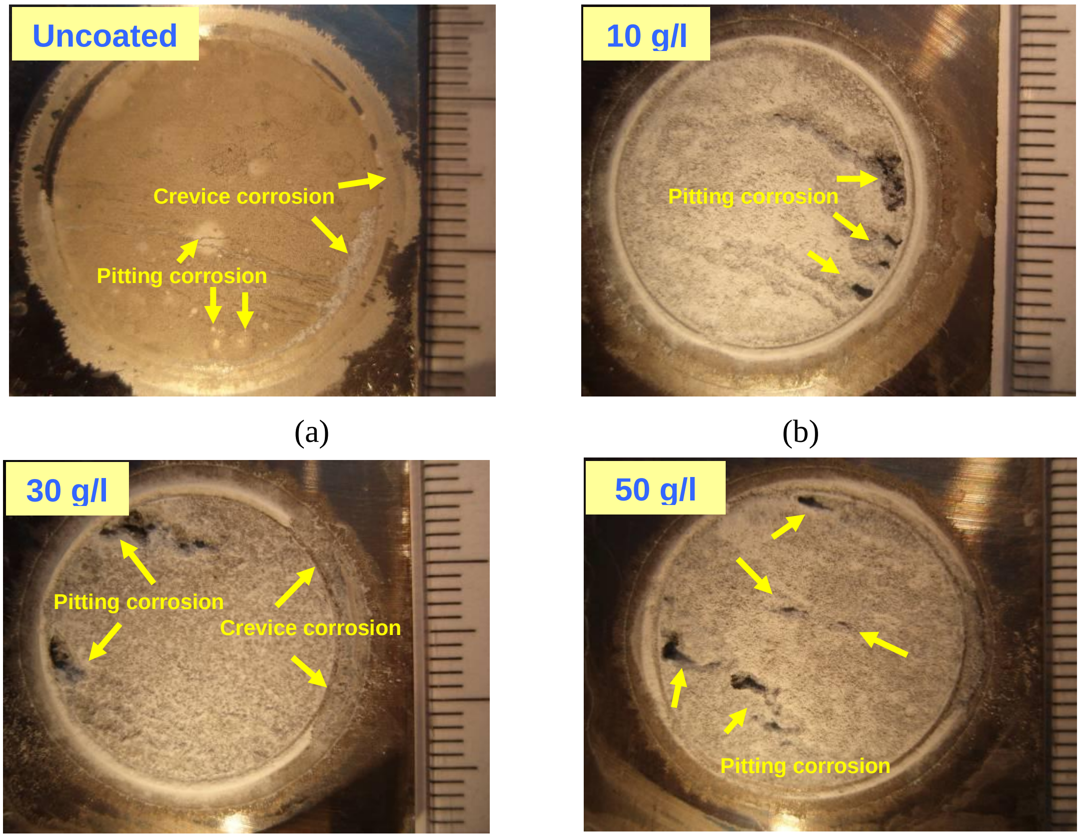
Macroscopic images were taken using digital optical metallographic microscope VHX-100K, KEYENCE, Japan, to investigate the types of corrosion produced on the substrate surfaces after seven days of immersion in 3.5% NaCl solution.

3. RESULTS AND DISCUSSION

3.1. Microscopic examination and visual inspection

(a) Elektron 21 alloy without vanadia coatings

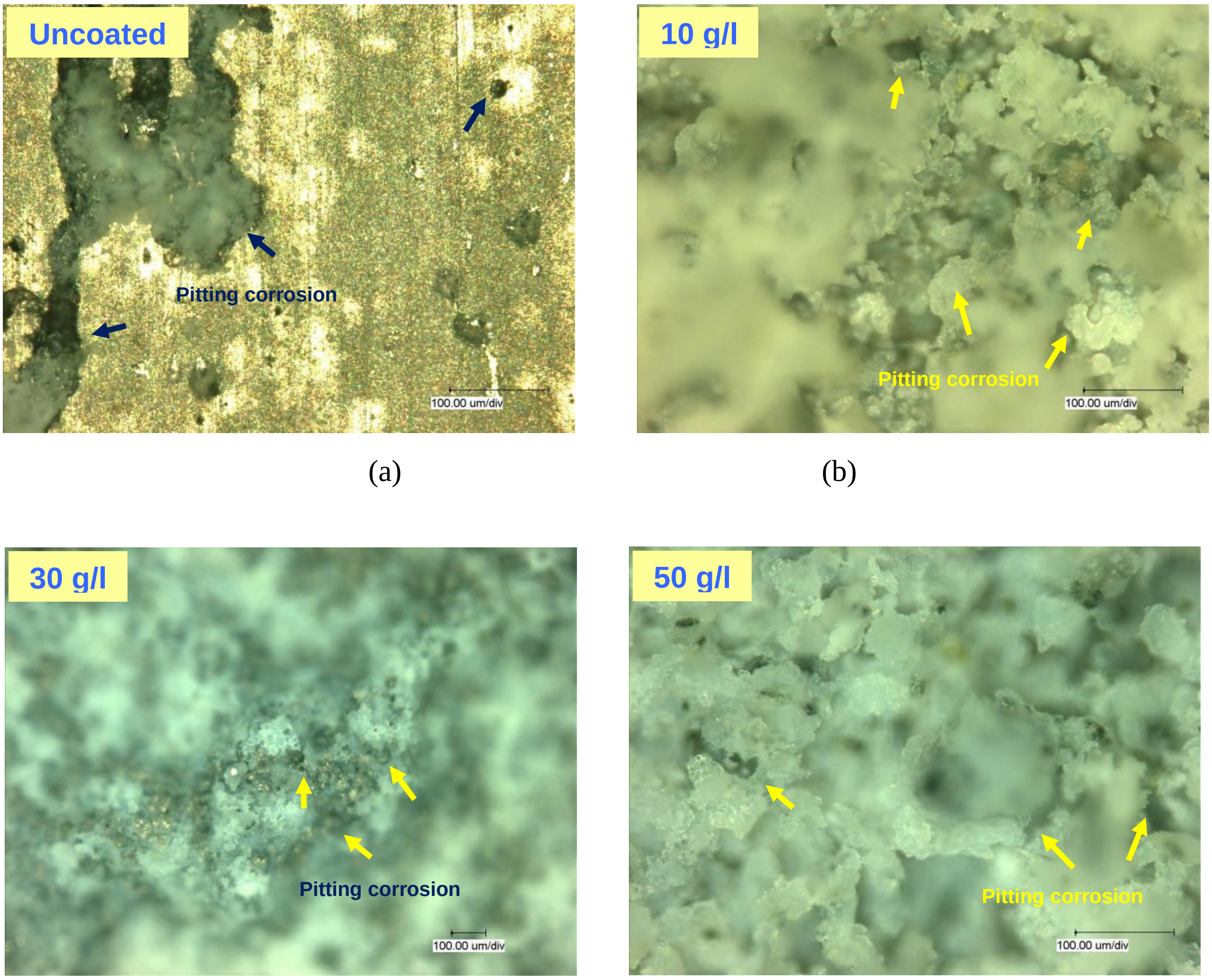
Visual inspection, macroscopic (Fig.1) and microscopic (Fig. 2) examination of the as-polished (uncoated) Elektron 21 alloy samples immersed for one week in 3.5% NaCl solution open to air and at room temperature showed severe crevice and general corrosion in addition to some tiny pits as illustrated in Fig. 1 and 2.



(a) (b)

(c) (d)

Figure 1. Macroscopic images for Elektron 21 alloy samples uncoated and coated with vanadia at different concentrations after seven days of free immersion in 3.5 % NaCl solution. Image (a) focuses on the crevice and general corrosion in addition to tiny pits for the uncoated samples. Images (b, c and d) focus on the severe pitting corrosion after vanadia coatings



(a) (b)

(c) (d)

Figure 2. Microscopic images for Elektron 21 alloy samples treated with vanadia at different concentrations after seven days of free immersion in 3.5 % NaCl solution. The images show some examples of pitting corrosion for uncoated and vanadia coated samples.

Such unexpected and limited corrosion resistance obtained from the newly developed Elektron 21 was the key issue behind the attempt to apply our vanadia coatings that were designed earlier and provided superior corrosion resistances with a self-healing functionality for several Mg and Al alloys in chloride containing solution [10-17].

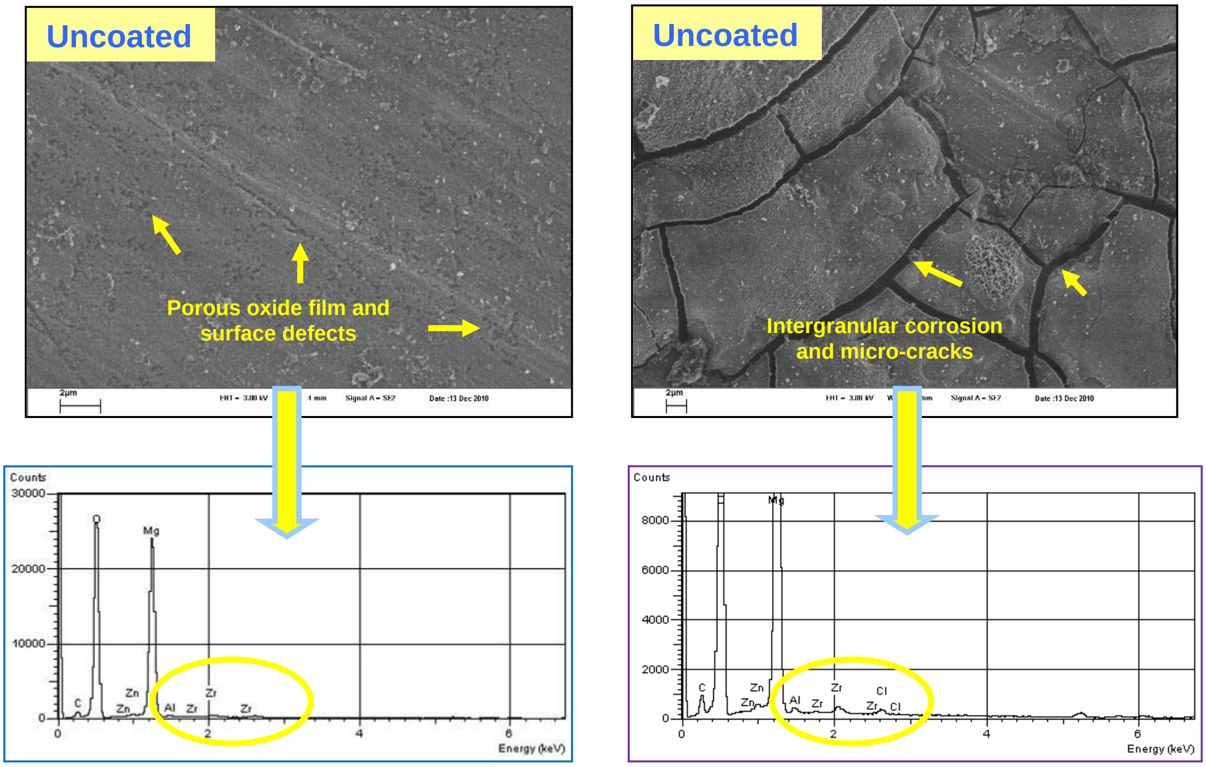
(a) Elektron 21 alloy coated with vanadia

Elektron 21 samples coated with vanadia at different concentration (10, 30 and 50 g/l) are shown in Figs. 1 and 2. The resistance to crevice and general corrosion improved. However, a remarked decrease in the pitting corrosion resistance was observed for all the samples coated vanadia. The depth and the size of pits increased dramatically after vanadia coatings (Figs 1b, c, d and 2b, c, d). The dramatic decrease in the corrosion resistance of Elektron 21 alloy after vanadia coating can be explained in the light of formation of two (or more) different oxides one from the coating layer (vanadium oxide) and the other from the alloying elements (mainly neodymium, zirconium oxides) when the corrosive solution diffuses through the upper layer. Formation of two (or more) different oxides makes the surface film inhomogeneous and hence water can easily diffuse through the pores among the oxide particles causing filiform and pitting corrosion.

3.2. SEM-EDS micrograph examination

(a) Elektron 21 alloy without vanadia coatings

SEM micrographs of the uncoated Elektron 21 alloy before corrosion showed a porous oxide of magnesium and zinc enriched with zirconium (Fig. 3a).



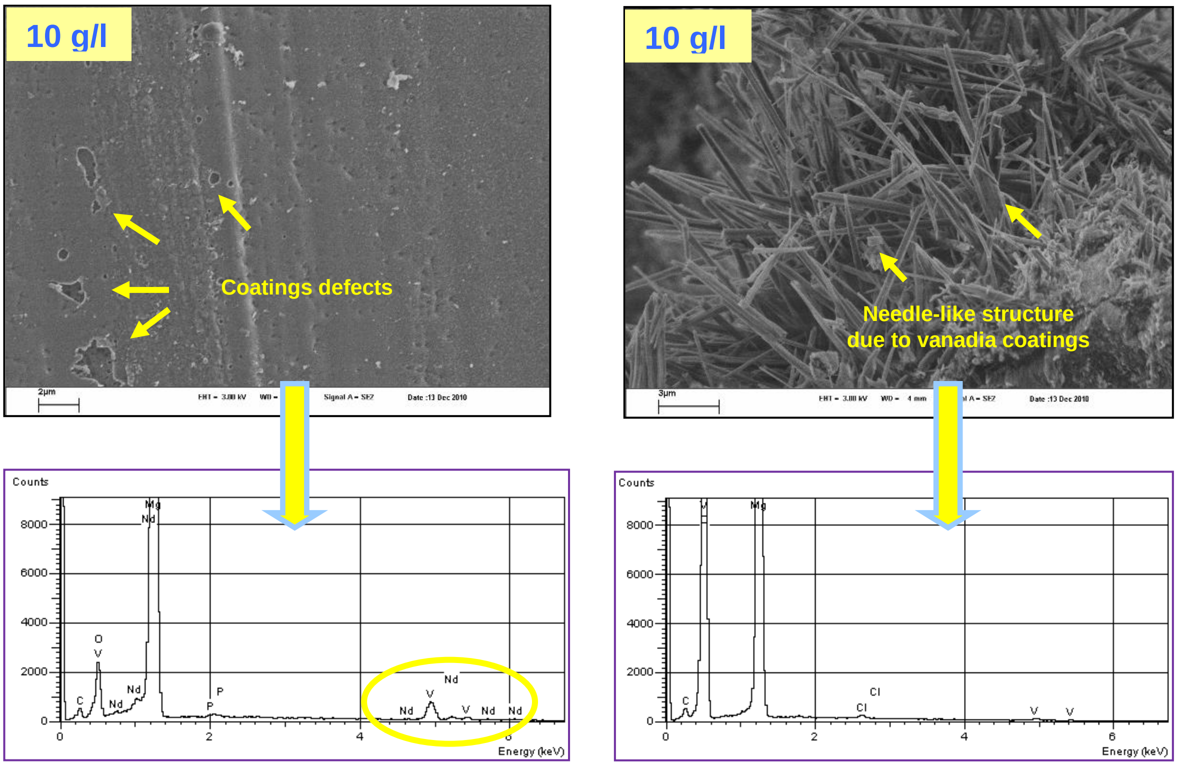
(a) (b)

Figure 3. SEM-EDS for the uncoated Elektron 21 alloy samples before (left) and after (right) one week of corrosion in 3.5 % NaCl solution. The images focus into the surface defects and the porous oxide film formed at the surface before corrosion and the micro-cracks and intergranular attack due to corrosion.

After one week of immersion in corrosive NaCl solution, a network like micro-cracked surface was observed for the uncoated Elektron 21 alloy samples (Fig. 3b). The occurrence of micro-cracks may be attributed to intergranular corrosion and selective dissolution of one (or more) of the alloying elements.

(b) Elektron 21 alloy coated with vanadia

The Elektron 21 alloy samples coated with vanadium showed relatively dense vanadium-rich magnesium oxide layers before corrosion.



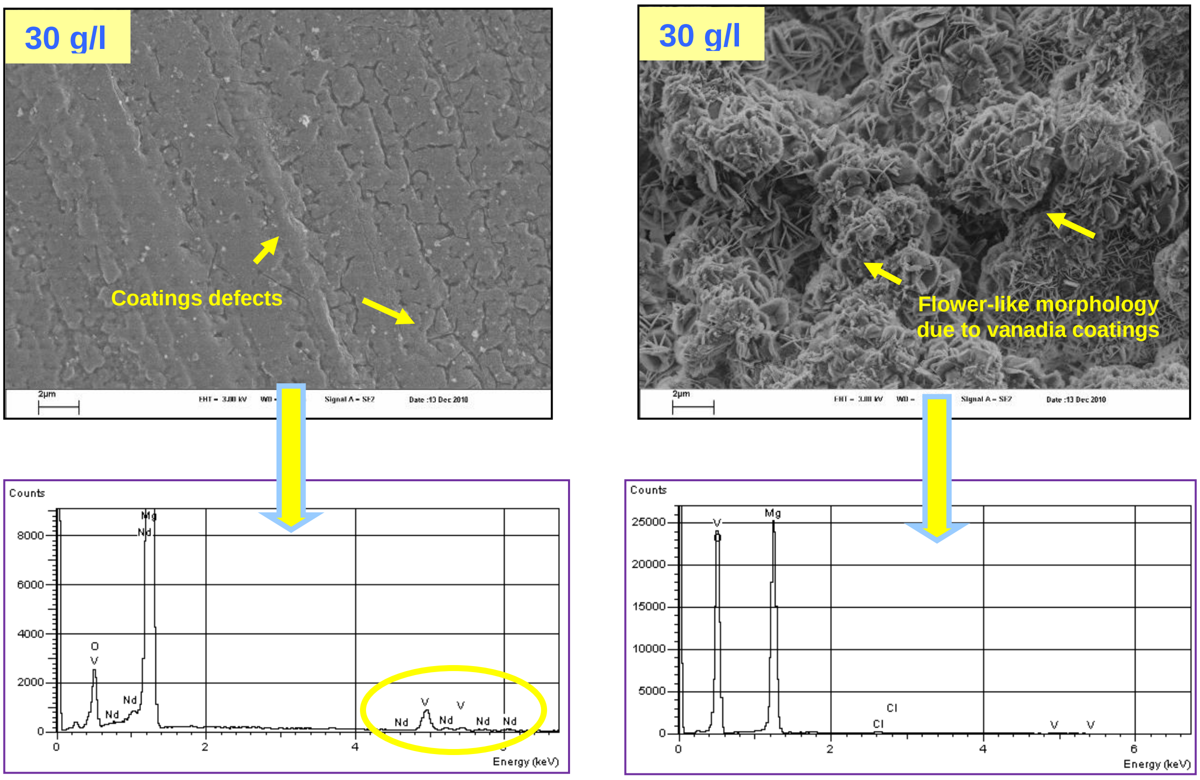
(a) (b)

Figure 4. SEM-EDS for the vanadia coated (10 g/l) Elektron 21 alloy samples before (left) and after (right) one week of corrosion in 3.5 % NaCl solution. The images focus into the coatings defects before corrosion and the formation of needle-like structure of vanadia oxide.

The coating distribution improved with increasing the vanadia coatings concentration as shown in Figs. 4a, 5a and 6a. Accordingly, the best surface coatings distribution with less surface defects and crack-free obtained from the samples coated with 50 g/l vanadia concentration (Fig. 6a).

After one week of immersion of the vanadia coated samples in NaCl solution, a dense vanadia-rich oxide layer formed at the magnesium substrate. Diluted vanadia coatings (10 g/l) showed an oxide layer of a needle-like structure (Fig. 4b). On the other hand, a flower-like morphology was observed due to concentrated (30 and 50 g/l) vanadia coatings (Figs 5b and 6b). The chemistry behind changing the morphology of the vanadia coatings from needle-like structure to flower-like morphology is not so clear and may be due to conversion of the oxidation state of vanadium oxide as a function of vanadia concentration. Moreover, the presence of some alloying elements (such as Nd as detected by EDS) may act as a catalyst to enhance the conversion of vanadium from an oxidation state to another.

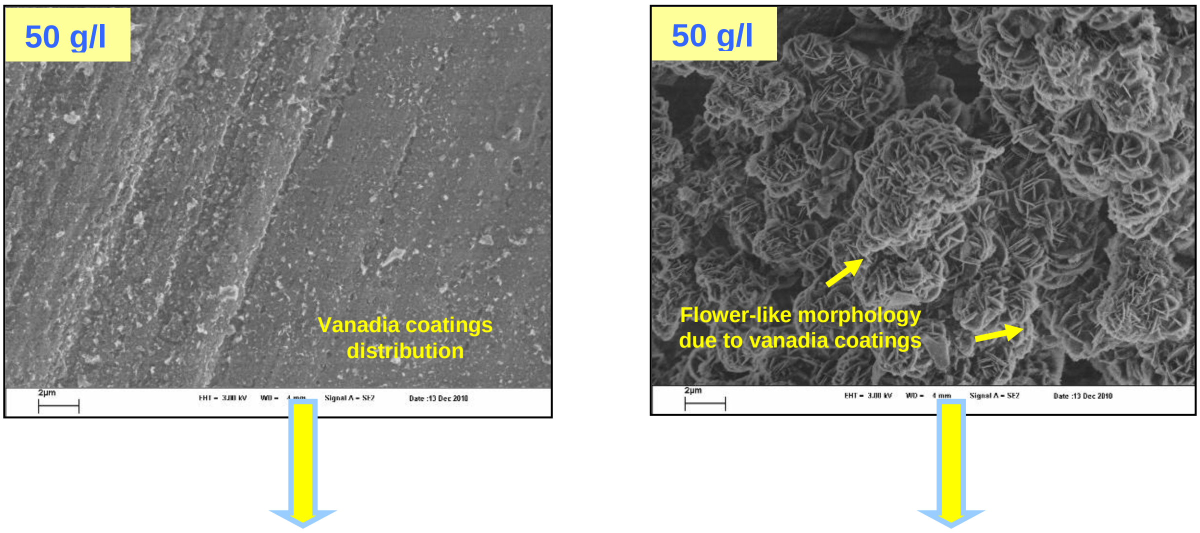
Microprobe analysis using energy dispersive spectrometry, EDS, (Figs. 3, 4, 5 and 6) revealed presence of zirconium (and absence of Nd) in the uncoated samples. Interestingly, no zirconium peaks were identified for the vanadia coated samples and few peaks of Nd were observed instead.

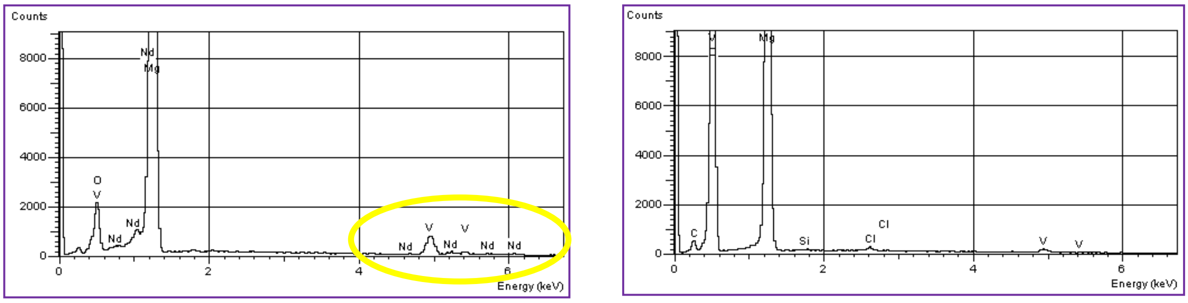


(a) (b)

Figure 5. SEM-EDS for the vanadia coated (30 g/l) Elektron 21 alloy samples before (left) and after (right) one week of corrosion in 3.5 % NaCl solution. The images focus into the coatings defects before corrosion and the formation of flower-like morphology of vanadia oxide over the localized corrosion areas.

The presence of Zr and absence of Nd in uncoated samples, and the of absence Zr and presence of Nd in the vanadia coated samples put a lot of question marks about the chemistry of oxides formation in the coated and uncoated samples.





(a) (b)

Figure 6. SEM-EDS for the vanadia coated (50 g/l) Elektron 21 alloy samples before (left) and after (right) one week of corrosion in 3.5 % NaCl solution. The images focus into the coatings defects before corrosion and the formation of flower-like morphology of vanadia oxide over the localized corrosion areas

The sharp drop in the pitting corrosion resistance of the samples coated with vanadia can now be explained by the inhomogeneity of the outer layer due to formation of different oxides of vanadium, neodymium, zinc and zirconium. Each of these oxides has a definite potential. Changing the local potential at the outer layer enhances the formation of localized electrochemical cells which is the main reason behind increasing the pitting corrosion after applying vanadia coatings.

3.3. Electrochemical impedance spectroscopy:

The corrosion behavior of Elektron 21 alloy samples uncoated or coated with vanadia at different concentrations 10, 30 and 50 g/l was investigated in corrosive 3.5% NaCl solution. According to Nyquist and Bode plots (Fig 7a and b), the highest surface resistance obtained from the uncoated samples (2.1x10^3 Ω.cm^2).

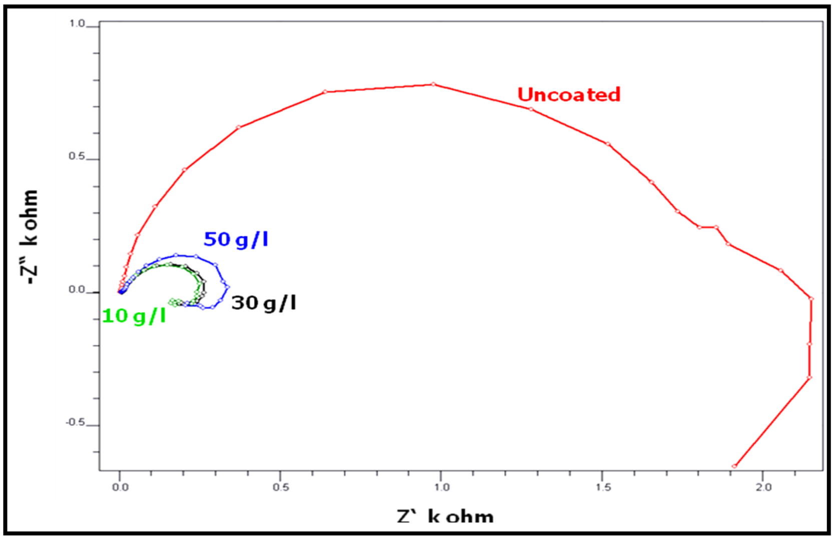


Figure 7a. Nyquist plots for uncoated and vanadia coated magnesium Elektron 21 alloy samples (with different vanadia concentrations) after one week in 3.5 %NaCl solution

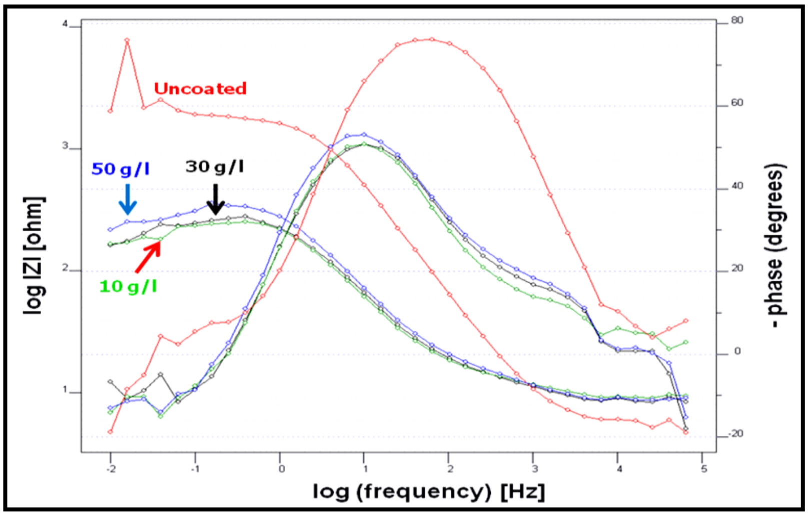


Figure 7b. Bode plots for uncoated and vanadia coated magnesium Elektron 21 samples (with different vanadia concentrations) after one week in 3.5 %NaCl solution

Surprisingly, vanadia coatings has an adverse effect on the overall surface resistance as they failed to provide any kind of protection against localized corrosion. The surface resistances due to vanadia coatings were $0.20x10^3$ Ω.cm^2, $0.25x10^3$ Ω.cm^2, and $0.35x10^3$ Ω.cm^2 for 10, 30 and 50 g/l vanadia coatings respectively.

Moreover, unlike the self healing effect that has been observed due to vanadia coating for many magnesium and aluminum alloys studied before [7-17], vanadia coatings over the advanced magnesium Elektron 21 alloy weren't able to show any sign self-healing functionality or corrosion inhibition. Such behaviour can be explained in the light of the surface inhomogeneity due to formation of multi oxides that can result in loosing vanadia coatings their self-healing property and inhibitive effect.

Increasing the vanadia concentration from 10 g/l to 50 g/l has a relative positive effect on improving the surface resistance, coating distribution and surface roughness but the overall surface resistance is still less than the uncoated samples.

This result confirms the previous observations of SEM, optical microscopy and visual inspection where the depth and the size of pits observed from due to vanadia coatings are much higher than the uncoated ones. Decreasing the pitting corrosion resistance after vanadia coatings confirms the adverse effect of vanadia in presence of other oxides formed from the alloying elements (Zr, Nd, Zn..etc). Such inhomogeneous layer will act as an electrochemical cell where the oxide(s) of less potential will act as cathode and the oxide(s) of higher potential will act as anode and consequently, the pitting corrosion increases as shown before.

4. CONCLUSION

The advanced magnesium Elektron 21 substrate is the only magnesium alloy compared with several other Al and Mg alloys studied before that showed an adverse localized corrosion resistance in chloride media after vanadia coatings.

The formation of multi oxides layer of vanadia in addition to Zr, Nd, Zn (present as alloying elements in Elektron 21) at the surface results in the inhomogeneity of the coating which enhances originating cathode/anode electrochemical cell.

Based on the surface examination, EIS and polarization measurements, the samples treated with 50 g/l vanadia solution showed a better corrosion resistance after seven days of immersion in NaCl solution compared with 10 and 30 g/l but still less than the uncoated samples.

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