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Electropolymerization and Characterization of Poly-N-methylpyrrole Coatings on AZ91D Magnesium Alloy

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We report the growth of a poly-N-methylpyrrole coating on a Mg alloy AZ91D in aqueous sodium salicylate solution using cyclic voltammetry (CV). The electropolymerization of poly-N-methylpyrrole coating was carried out in a one step process without any further pretreatment of the AZ91D surface. The polymeric coatings were analyzed using x-ray photoelectron spectroscopy (XPS), time-of-flight secondary-ion-mass-spectrometry (ToF-SIMS) and scanning electron microscopy (SEM). The adhesion of poly-N-methylpyrrole coatings was tested applying ASTM D33359-09 standard, which showed good adhesion properties. Electrochemical impedance spectroscopy (EIS) in aqueous 0.1 M Na_2SO_4 solution indicates improved corrosion resistance of the coated samples compared to the bare AZ91D surface; the efficiency of protection was found to depend on the concentration of sodium salicylate used during electropolymerization.

Keywords: magnesium, AZ91, coating, pyrrole, electropolymerization

1. INTRODUCTION

As an important part of the human organism, magnesium and its alloys are considered to be suitable biodegradable implant materials [1, 2]. Despite the good mechanical properties and the superior biocompatibility, the application of magnesium alloys as implant materials suffers of their too fast corrosion rate [3-6]. Due to the high dissolution rate, the H_2 gas evolution and the pH increase in the vicinity of corroding magnesium surfaces in aqueous solutions, the corrosion properties have to be improved for medical applications, e.g. by coating the surface. Many different methods were introduced in the past, as has been summarized in a recent review [7]. For successful application of magnesium and its alloys in human body environment two main problems have to be solved: First is to control the dissolution during the coating process, and the second is to control the corrosion in the human body environment.

As a promising coating technology, various conducting polymers (CPs) have been applied to different metal surfaces [8]. Although the application of CP coatings can be seen critically [9, 10], CPs enhance the corrosion resistance of the coated surface [11]. Amongst these CPs, pyrrole and its derivatives are promising candidates for corrosion protection of biomedical metallic devices, due to their biocompatibility, stable oxidized state and the release of dopant ions. Polypyrrole coatings have been electropolymerized on various substrates such as copper [12], iron [13], aluminum [14], zinc [15, 16] and magnesium [17-19]. Most coating methods of reactive metals, if carried out in aqueous solutions, need a pretreatment to hinder corrosion during the initiation and growth of the protection layer. By using an aqueous sodium salicylate solution, Hermelin et al. [20] introduced a direct electropolymerization of a polypyrrole layer on zinc. Using the advantage of sodium salicylate, Turhan et al. [17] successfully coated AZ91D with polypyrrole in a one step process utilizing cyclic voltammetry. Despite promising results such as the improved corrosion resistance and the release of corrosion inhibiting salicylate for polypyrrole coated AZ91D in simulated body fluid [18], the adhesion of the layer needs improvement. One possible way to modify the properties of the coating, especially the adhesion, is to change the monomer, for instance to explore N-methylpyrrole as biocompatible coating. Although the nucleation and growth of poly-N-methylpyrrole layers on substrates such as copper [21], platinum [22] and various steels [23-27] already provided adherent layers and improvement of the corrosion properties, no research has been published for poly-N-methylpyrrole coatings on magnesium yet.

In the present study the first step of developing a biodegradable coating for AZ91D is investigated by directly electrochemically polymerizing a poly-N-methylpyrrole coating on AZ91D from aqueous salicylate solution for the first time. The corrosion properties were studied using Na_2SO_4 solution as corrosive medium for preliminary investigation of improvement of the corrosion behavior of AZ91D by these coatings.

2. EXPERIMENTAL

An AZ91D sheet, a Mg alloy containing 9 wt% Al and 1 wt% Zn, was cut in rectangular pieces (2cm x 2cm x 0,5cm) and ground with 1200 SiC abrasive paper (Struers) using ethanol as lubricant. Afterwards the samples were cleaned with ethanol in an ultrasonic bath for 10 min, rinsed with ethanol and dried with hot air. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out with Autolab PGSTAT 30 using Nova^{TM} software in a three electrode system utilizing a platinum sheet (1,7cm x 1,7cm x 0,01cm) as counter electrode and Ag/AgCl (3 mol/l KCl) as reference electrode. To expose the same area of surface to the electrolyte, the sample was pressed against a bottom hole in the cell, sealed with a PTFE O-ring, and contacted with a copper plate. For synthesizing N-methylpyrrole layers on AZ91D, CV was performed in the potential range of 0 and 1.2 V with a sweep rate of 20 mV/s for 20 cycles using aqueous 0.1 M methylpyrrole (Sigma) solution with different sodium salicylate (Sigma) concentrations. Afterwards, each sample was rinsed with high purity water and dried with nitrogen. EIS measurements with a perturbation signal of ± 10 mV and 10 measurement points per decade in a frequency range of 100 kHz to 10 mHz in a 0.1 M Na_2SO_4 (Sigma) aqueous solution after 30 min of OCP were carried out to characterize the coated surface. All experiments were carried out three times and the average is presented with respect to the surface. The chemical composition of the coated surface was analyzed using X-ray induced photoelectron spectroscopy (XPS) Phi-5600, using Al Kα radiation. Additionally negative and positive static time-of-flight secondary-ion-mass-spectrometry (ToF-SIMS) was used to investigate the composition of the coating. ToF-SIMS measurements were performed on a ToF.SIMS V spectrometer (ION.TOF, Münster). A pulsed 25 keV Bi_3^+ liquid-metal ion beam was rastered over a 500 x 500 μm^2 area to irradiate the sample. Spectra were recorded in high mass resolution mode ($m/\Delta m > 8000$ at ^{29}Si). The surface morphology was investigated with a field emission scanning electron microscope (Hitachi, FE-SEM S-4800) with an acceleration voltage of 10 kV using a cold field emitter. Adhesion tests were carried out following ASTM D3359-09 “Standard Test Methods for Measuring Adhesion by Tape Test” on poly-N-methylpyrrole and polypyrrole coated AZ91D. The polypyrrole coatings for reference measurements were synthesized following the method of Turhan et al. [18] with CV in the potential range of 0 to 1 V with a sweep rate of 20 mV/s for 20 cycles in 0.1 M aqueous pyrrole (Sigma) containing 0.5 M sodium salicylate (Sigma).

3. RESULTS AND DISCUSSION

3.1. Electropolymerization and characterization of N-methylpyrrole on AZ91D

AZ91D was coated with poly-N-methylpyrrole using cyclic voltammetry in the potential range of 0 – 1.2 V and a sweep rate of 20 mV/s. The potential range was chosen according to Asavapiriyanont et al. [22], who reported the potential range of 0 – 1.2V to be best for electropolymerization of N-methylpyrrole on Pt. Formation of a dark brown coating on AZ91D was observed using aqueous 0.1M N-methylpyrrole solution containing 0.1M sodium salicylate as electrolyte. Cascalheira et al. and Hermelin et al. showed the formation of a metal salicylate film on the surface, decreasing the dissolution of the metal and positively influencing the formation of polypyrrole on copper [28] and zinc [29], and determined the oxidation peak at around 1 V.

Fig. 1a shows the cyclic voltammogram of AZ91D in 0.1M aqueous sodium salicylate solution between 0 – 1.2 V with a sweep rate of 20 mV/s for 20 cycles. The first cycle (inset fig. 1a) shows a peak between 0 and 0.5 V which is related to shift of equilibrium in the electrochemical system resulting in an increased current flow by application of a start potential of 0 V (i.e., a direct potential step from the open-circuit potential of -1.6 V to 0 V results in high anodic current densities). These peaks can also be seen in the second cycle. With ongoing cyclic voltammetry these peaks disappear. The increasing current density at 1.2 V and the decreasing current density at 0 V, as well as the overall high current densities measured during the cyclic voltammetry are related to active dissolution of the alloy. Although Cascalheira et al. [30] reported the sodium salicylate oxidation peak to be at around 1 V, this specific peak cannot be defined. Turhan et al. [17] also pointed out that the oxidation peak of sodium salicylate on AZ91D occurs around 1 V. The peak may not be distinguished in our study because of the dissolution of the magnesium alloy and/or the salicylate concentration of 0.1 M is too low as compared to [17, 30].

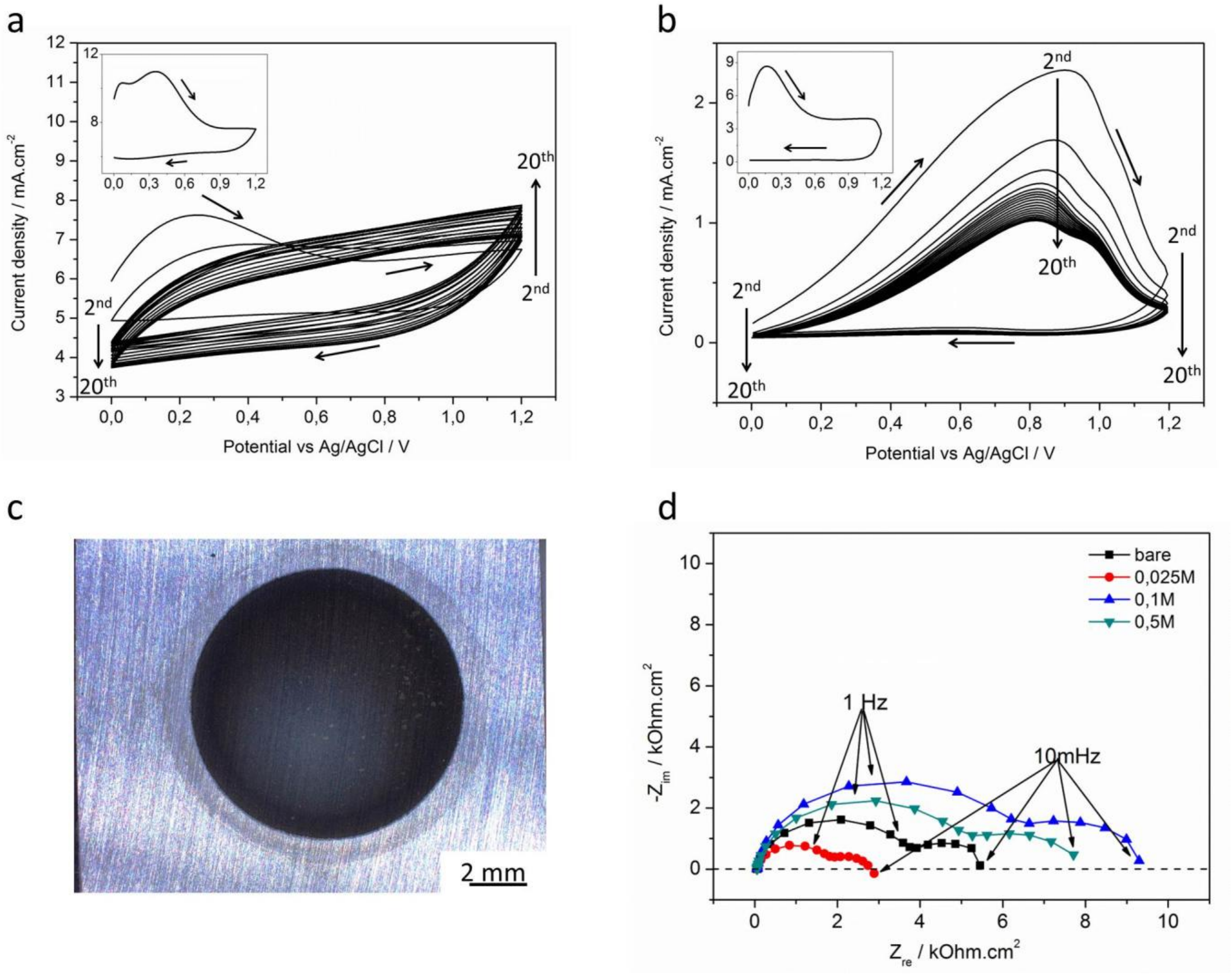

Figure 1. a) Cyclic voltammogram of AZ91D in aqueous 0.1M sodium salicylate solution, b) cyclic voltammogram of AZ91D in aqueous 0.1M sodium salicylate solution with addition of 0.1M N-methylpyrrole, c) macroscopic image of the obtained poly-N-methylpyrrole coating on AZ91D surface, d) Nyquist plots of EIS of bare compared to poly-N-methylpyrrole coated AZ91D surface in aqueous 0.1M N-methylpyrrole solution containing different sodium salicylate concentrations

Figure 1b shows the electropolymerization of N-methylpyrrole on AZ91D in sodium salicylate solution. A dark brown coating as shown in fig. 1c is grown on the AZ91D surface. With the addition of 0.1M N-methylpyrrole to the electrolyte a current drop is observed at the beginning of the reversed scan in the first cycle (inset fig. 1b). The peak between 0 and 0.5 V is also obtained, comparable to fig. 1a during the first cycle. After the first cycle the current density remarkably drops to lower values due to the formation of a protective layer on the surface. The occurring oxidation peak between 0.5 and 1.1

V is related to poly-N-methylpyrrole nucleation and growth [22]. With increasing cycling numbers the current density at 1.2 V decreases, which is correlated to the step-by-step formation of a protecting poly-N-methylpyrrole layer on the surface. The reverse parts of the cycles indicate that the oxidation of poly-N-methylpyrrole is not reversible. Again no sodium salicylate peak can be observed, probably due to overlapping with the oxidation peak of N-methylpyrrole.

Fig. 1d compares the electrochemical impedance spectroscopy of the bare AZ91D surface with poly-N-methylpyrrole coatings produced with different sodium salicylate concentrations in 0.1M Na_2SO_4. The bare AZ91D surface shows two capacitive loops with an inductive loop, this type of impedance spectra have been frequently reported for actively corroding Mg alloy surfaces [31, 32]. The inductive loop is typical for actively dissolving metal surfaces, as discussed in [33, 34]. The impedance spectra of poly-N-methylpyrrole coated samples indicate similar electrochemical behavior as compared with AZ91D coated with polypyrrole [17, 18], namely poly-N-methylpyrrole coatings also show two capacitive loops but no inductive loop. The polarization resistance of poly-N-methylpyrrole coatings produced with 0.1 M sodium salicylate shows the biggest increase of the polarization resistance. The methylpyrrole coating obtained with 0.025M sodium salicylate shows even a lower corrosion resistance than that of the bare AZ91D surface; this may be due to roughening of the surface by substrate dissolution during the coating process, when an insufficient amount of the inhibiting salicylate is present in the electrolyte. In contrast to AZ91D, the poly-N-methylpyrrole (prepared with 0.1M sodium salicylate) coated surface shows no inductance, and the increase in polarization resistance indicates that the coating acts as a barrier layer against dissolution of the surface, as described in [35]. The EIS measurements clearly reveal that the concentration of Na-salicylate in the electropolymerization electrolyte is a key factor for successful coating preparation, and a concentration of 0.1 M leads to most promising properties of the poly-N-methylpyrrole layer for corrosion protection of AZ91D. As Na_2SO_4 is a relatively non-aggressive electrolyte, it is here used as a model electrolyte for a first check of the general improvement of the corrosion properties of AZ91D by the different coatings. For possible biomedical applications, the protective effect of the coating has to be investigated in chloride containing solutions or simulated body fluid.

3.2. Surface analysis with SEM, XPS and ToF-SIMS

The poly-N-methylpyrrole coating was investigated using SEM. Figure 2a shows the transition of uncoated to poly-N-methylpyrrole coated AZ91D. A non-uniform layer is visible on the coated section. Figure 2b shows a magnification of the coating of figure 2a, revealing the porous structure of the poly-N-methylpyrrole coating. The formed layer is very thin, as the grinding striations are still visible in the pores. Also a few cracks can be seen in the pores, indicating presence of a thin layer in the porous sites. The obtained layer has a platelet like structure in contrast to the already reported cauliflower like structures for poly-N-methylpyrrole coatings [21, 23, 27].

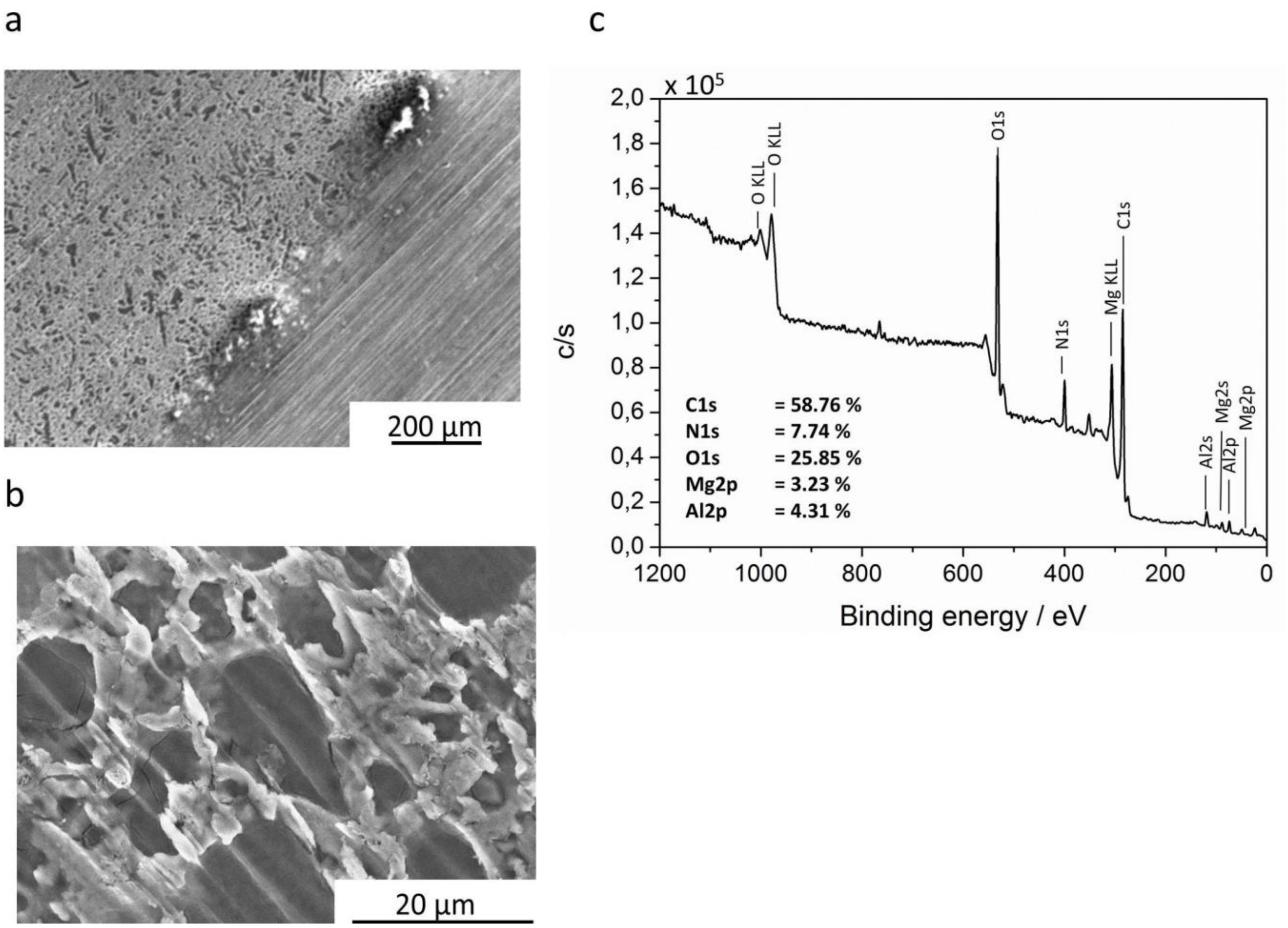

Figure 2. a and b) SEM images and c) XPS spectra of poly-N-methylpyrrole coated AZ91D surface

The XPS survey spectrum demonstrates that the surface consists mainly of C (58.76 %), O (25.85%) and N (7.74%), as shown in figure 2c. The presence of N on the surface is a good indication for the successful coating of AZ91D with N-methylpyrrole. The low Mg (3.23 %) and Al (4.31 %) signals also indicate surface coverage by a poly-N-methylpyrrole layer. Compared to [17] the XPS results are similar and demonstrate the successful coating of AZ91D.

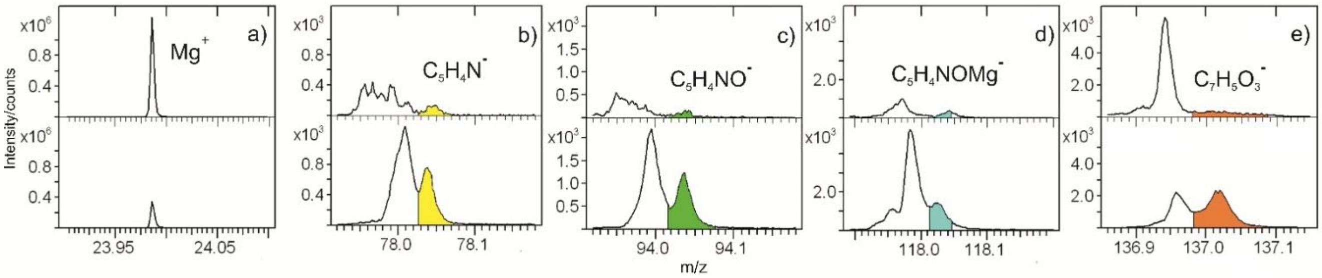

Figure 3. ToF-SIMS spectra of uncoated (top) and poly-N-methylpyrrole coated (bottom) AZ91D surface, a) Mg^+, b) $C_5H_4N^-$, c) $C_5H_4NO^-$, d) $C_5H_4NOMg^-$, e) $C_7H_5O_3^-$

In line with the XPS analysis, ToF-SIMS measurements indicate the successful coating of AZ91D with poly-N-methylpyrrole. Figures 3a-f show the ToF-SIMS spectra for bare (top) and poly-N-methylpyrrole coated AZ91D (bottom) surface.

The colored parts of the graphs show the signals related to the fragments of N-methylpyrrole. Figure 3a shows the decrease of the Mg^+ signal due to surface coverage with N-methylpyrrole. Figure 3b and c show the fragments $C_5H_4N^-$ and $C_5H_4NO^-$ belonging to N-methylpyrrole, which appear only on the coated sample. Furthermore the $C_5H_4NOMg^-$ fragment shown in Figure 3d suggests N-methylpyrrole being covalently bonded to magnesium on the surface. Figure 3e shows the molecular fragment of salicylate $C_7H_5O_3^-$, probably being incorporated into the poly-N-methylpyrrole coating. Similar to the findings by Turhan et al. [17] ToF-SIMS demonstrates the presence of N-methylpyrrole and sodium salicylate on the AZ91D surface and indicates a successful poly-N-methylpyrrole coating by direct electropolymerization.

3.3. Adhesion test of polypyrrole and poly-N-methylpyrrole with ASTM D33359-09 norm

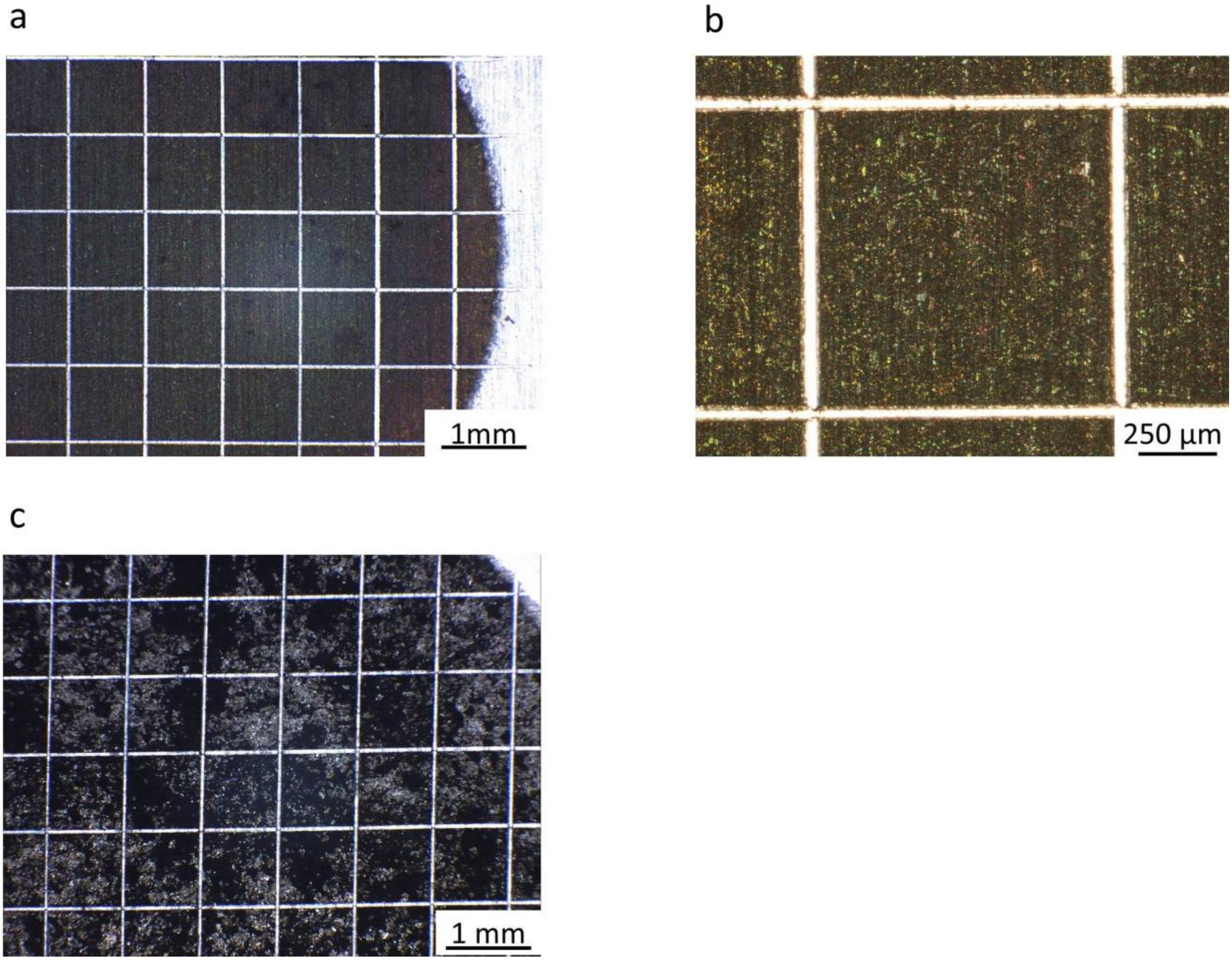

Figure 4. Microscopic image of a) poly-N-methylpyrrole, b) magnification of (a), c) polypyrrole coated AZ91D surface tested with ASTM D33359-09 standard regarding to adhesion of the layers

The adhesion of poly-N-methylpyrrole coatings on AZ91D was tested by application of the ASTM D33359-09 norm. Therefore the coating was scratched, as shown in figure 4, and subsequently the coating was covered with tape, which was pulled off. Figure 4a and 4b show the poly-N-methylpyrrole coating and figure 4c shows a polypyrrole film after adhesion testing. The polypyrrole layer was electropolymerized using the approach of Turhan et al. [18]. The surfaces then were classified according to ASTM standard. The poly-N-methylpyrrole coating exhibits no to nearly no removal of the layer. Therefore it is assigned to category 5B-4B, corresponding to a removal of 0 – 5 % of the coating. Polypyrrole shows delamination of the edges as well as on the centers of the squares. These results are similar to Turhan et al. provided in [18] applying a "tape test" without any standardization. Thus the adhesion of the polypyrrole layer is assigned to category 3B-2B, corresponding to a removal of 5 – 35 % of coated area. Poly-N-methylpyrrole coating on AZ91D hence displays significantly better adhesion to the surface than the polypyrrole coatings. The origin of this behavior, which may be related to different types of interfacial reactions between the alloy surface and the different polymer molecules, needs to be further investigated.

4. CONCLUSIONS

AZ91D was successfully coated with N-methylpyrrole by electropolymerization using cyclic voltammetry with a potential range between 0 – 1.2 V and a sweep rate of 20 mV/s for 20 cycles in aqueous 0.1M N-methylpyrrole solution. A thin dark brown layer was grown on the surface. EIS in aqueous 0.1M Na_2SO_4 solution revealed the best corrosion performance for a poly-N-methylpyrrole coating electropolymerized with addition of 0.1M sodium salicylate in the electrolyte as corrosion inhibitor and dopant. SEM images revealed a porous platelet like structure of the poly-N-methylpyrrole coating. XPS showed the presence of N atoms on the surface, demonstrating surface coverage by N-methylpyrrole. In addition, ToF-SIMS spectra showed fragments of sodium salicylate and N-methylpyrrole what further demonstrates the successful coating of AZ91D. Adhesion tests of poly-N-methylpyrrole and polypyrrole layer performed after ASTM D33359-09 showed significantly improved adhesion of poly-N-methylpyrrole compared to polypyrrole on AZ91D.

Future work on tailoring the corrosion behavior of Mg alloys by poly-N-methylpyrrole coatings will be on the one hand side the exploration of the electropolymerization parameters in view of optimization of the protective nature of the coating. On the other hand, performance of these coatings under different type of environments, including biodegradation studies, will be carried out.

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References

1. G.L. Song and S.Z. Song, *Adv Eng Mater*, 9 (2007) 298
2. F. Witte, N. Hort, C. Vogt, S. Cohen, K.U. Kainer, R. Willumeit and F. Feyerabend, *Curr Opin Solid St M*, 12 (2008) 63
3. S. Virtanen, *Mater Sci Eng B-Adv*, 176 (2011) 1600
4. G.L. Song and A. Atrens, *Adv Eng Mater*, 1 (1999) 11
5. M.S. Killian, V. Wagener, P. Schmuki and S. Virtanen, *Langmuir*, 26 (2010) 12044
6. G.L. Song and A. Atrens, *Adv Eng Mater*, 5 (2003) 837
7. H. Hornberger, S. Virtanen and A.R. Boccaccini, *Acta Biomater*, 8 (2012) 2442
8. S. Biallozor and A. Kupniewska, *Synthetic Met*, 155 (2005) 443
9. M. Rohwerder and A. Michalik, *Electrochim Acta*, 53 (2007) 1300
10. G. Williams and H.N. McMurray, *Electrochem Solid St*, 8 (2005) B42
11. D.E. Tallman, G. Spinks, A. Dominis and G.G. Wallace, *J Solid State Electr*, 6 (2002) 73
12. B. Duran, M.C. Turhan, G. Bereket and A.S. Sarac, *Electrochim Acta*, 55 (2009) 104
13. H.N.T. Le, B. Garcia, C. Deslouis and Q. Le Xuan, *Electrochim Acta*, 46 (2001) 4259
14. M.A. Arenas, L.G. Bajos, J.J. de Damborenea and P. Ocon, *Prog Org Coat*, 62 (2008) 79
15. M.H. Pournaghi-Azar and H. Nahalparvari, *Electrochim Acta*, 50 (2005) 2107
16. G. Paliwoda-Porebska, M. Rohwerder, M. Stratmann, U. Rammelt, L.M. Duc and W. Plieth, *J Solid State Electr*, 10 (2006) 730
17. M.C. Turhan, M. Weiser, M.S. Killian, B. Leitner and S. Virtanen, *Synthetic Met*, 161 (2011) 360
18. M.C. Turhan, M. Weiser, H. Jha and S. Virtanen, *Electrochim Acta*, 56 (2011) 5347
19. N. Sheng, M. Ueda and T. Ohtsuka, *Prog Org Coat*, 76 (2013) 328
20. E. Hermelin, J. Petitjean, S. Aeiyach, J.C. Lacroix and P.C. Lacaze, *Rev Metall-Paris*, 97 (2000) 1501
21. M.A. Raso, M.J. Gonzalez-Tejera, I. Carrillo, E.S. de la Blanca, M.V. Garcia and M.I. Redondo, *Thin Solid Films*, 519 (2011) 2387
22. S. Asavapiriyanont, G.K. Chandler, G.A. Gunawardena and D. Pletcher, *J Electroanal Chem*, 177 (1984) 245
23. W.C. Su and J.O. Iroh, *J Appl Polym Sci*, 71 (1999) 1293
24. J.O. Iroh and W.C. Su, *Synthetic Met*, 97 (1998) 73
25. W.C. Su and J.O. Iroh, *Electrochim Acta*, 44 (1999) 3321
26. J.O. Iroh and W.C. Su, *Electrochim Acta*, 46 (2000) 15
27. M.R. Mahmoudian, W.J. Basirun, Y. Alias and M. Ebadi, *Appl Surf Sci*, 257 (2011) 8317
28. A.C. Cascalheira, S. Aeiyach, J. Aubard, P.C. Lacaze and L.M. Abrantes, *Russ J Electrochem+*, 40 (2004) 294
29. E. Hermelin, J. Petitjean, J.C. Lacroix, K.I. Chane-Ching, J. Tanguy and P.C. Lacaze, *Chem Mater*, 20 (2008) 4447
30. A.C. Cascalheira and L.M. Abrantes, *Electrochim Acta*, 49 (2004) 5023
31. G. Song, A. Atrens, D. St John, X. Wu and J. Nairn, *Corros Sci*, 39 (1997) 1981
32. G. Baril, C. Blanc and N. Pebere, *J Electrochem Soc*, 148 (2001) B489
33. I. Epelboin, *J Electrochem Soc*, 117 (1970) 1052
34. I. Epelboin and R. Wiart, *J Electrochem Soc*, 118 (1971) 1577
35. M.I. Redondo and C.B. Breslin, *Corros Sci*, 49 (2007) 1765