Formation and corrosion protective effect of alkyl-phosphonate monolayers

Thesis of Ph.D. dissertation

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In memoriam Dr. Erika Kálmán,
my supervisor

1. Introduction and Objectives

On the basis of the report published by The World Corrosion Organization [Schmitt, 2009] in May 2009, the annual cost of corrosion worldwide is estimated to exceed $U.S. 1.8 trillion, which translates to 3 to 4 % of the Gross Domestic Product (GDP) of industrialized countries. In view of this numbers, any new method or procedure, which helps in blocking of corrosive processes, can be beneficial for the humanity. Coatings, paints, protective layers created with the help of nanosciences can be applied in the fight against corrosion.

The investigation of protective effects of alkyl-phosphonates against corrosion started at late Nineties at the Chemical Research Center of the Hungarian Academy of Sciences. Organic, ordered and compact thin layers can replace toxic and environmentally damaging inhibitors or coatings. With the use of these layers we can gain materials and energy savings. Alkyl-phosphonates replace the carcinogenic Cr^{6+} compounds [KVM, 2005]. According to the new European legislation the formerly used chromate conversion coating technique for temporary corrosion protection must be substituted by environmentally acceptable ones.

In the early stage of the research the main goal was to find the most suitable alkyl-phosphonate for corrosion protection [Felhősi, 2002]. Among the investigated compounds (1-hexyl-phosphonate /HePA/, 1-heptyl-phosphonate /HpPA/, 1-octyl-phosphonate /OcPA/ and 1-decyl-phosphonate /DPA/), the 1-octyl-phosphonate was found to be the most effective.

Based on these results, my research was focused on the detailed study of the formation, structure and corrosion protective effect of alkyl-phosphonate layers on previously passivated polycrystalline iron surface. The following questions were waiting for elucidation:

- How does the phosphonate layer form on the surface?
- How can the OcPA layer control the corrosion?
- What is the structure of the anticorrosive layer?

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[KVM, 2005] Környezetvédelmi és Vízügyi Minisztérium: 6/1. KvVM útmutató az elérhető legjobb technika meghatározásához a fémek és műanyagok felületkezelése terén, Budapest, 2005

[Felhősi, 2002] I. Felhősi, J. Telegdi, G. Pálinkás, E. Kálmán: *Electrochim. Acta* 47 (2002) 2335

2. Preparation and characterization of alkyl-phosphonate layers

Phosphonate layers were produced by immersion of the passivated iron specimens and mica model surface into the solution of 1-octyl-phosphonate for different time.

The formation, structure and corrosion protective effect of self-assembled alkyl-phosphonate layer were investigated by electrochemical, surface characterization and surface analytical techniques:

Surface tension measurement was used to make clear whether the phosphonate molecules are separately or in aggregates in the aqueous solution.

Layer formation of self-assembling molecules of alkyl-phosphonates was followed by *atomic force microscopy (AFM)*. The morphology of passive iron and its changes due to the phosphonation has been also investigated by AFM.

The protective layer formation of octyl-phoshonate and its effectiveness on passive iron surface were followed by *electrochemical impedance spectroscopy (EIS)*.

The structure and composition of the surface film on modified iron were determined with *^{57}Fe conversion electron Mössbauer spectroscopy (CEMS)* and *X-ray photoelectron spectroscopy (XPS)*.

Complementary measurements on the investigated system were made by *X-ray powder diffractometry (XRD)*, *scanning electron microscope (SEM)* equipped with *energy dispersed X-ray spectroscopy (EDS)* and *spectral ellipsometry*.

3. The theses of the Ph.D. dissertation

Results got by electrochemical, surface investigating and surface analyzing measurements are the following:

1. I have shown that the layer formed on the pre-passivated polycrystalline iron surface in 1-octyl-phosphonate solution is composed of Fe^{II} and Fe^{III} phosphonate. The phosphonate molecules bond through deprotonated head group to the substrate [1,2].

2. I have proved the importance of iron pre-passivation in borate buffer solution, which results in a gradual stabilization of the evolving self-assembled phosphonate layer. The whole passive potential range between -200 mV and +800 mV (vs. SCE) proved to be suitable for providing favorable conditions for phosphono group bounding onto the surface. I have shown that the shape of the nanosize oxide grains (formed during the pre-passivation of iron surface) changes due to the combined effect of the phosphonate layer formation and the metal dissolution process, which takes place at the edges of oxide grains [1,2,5].

3. I have proved the formation of monomolecular thick phosphonate layer on the pre-passivated iron surface in 1-octyl-phosphonate solution [1].

4. I have established that the 1-octyl-phosphonate monolayer created on the pre-passivated iron surface have corrosion protective effect (>98%), that proves the dense and compact structure of phosphonate layer [1].

5. I have firstly managed to successfully develop monomolecular thick phosphonate layer on atomically flat mica model surface in aqueous solution of 1-octyl-phosphonate. Strong interaction between the phosphonate functional head-group and the mica surface was proved by abrasion-resistant investigation. I have observed hexagonal lattice packing of 1-octyl-phosphonate molecules on mica model surface [4].

6. I have found the formation of amorphous iron during low energy ion bombardment on the surface previously covered by ^{57}Fe thin film. This was unexpected, up-to-now only energetic heavy ion irradiation of Fe film and sonochemical experiments resulted in amorphous iron formation. The decrease of relative occurrence of the amorphous iron by pre-passivation and phosphonation revealed that the amorphous iron can participate in chemical reactions with higher affinity than crystalline iron [2,3].

4. Possible industrial applications

The results presented in my Ph.D. dissertation can contribute to successful industrial applications of anticorrosion methods.

The ordered, compact and stable self-assembled monolayers can be applied for corrosion protection, for example as anticorrosion surface treatment for temporary protection or in the paint industry as surface modifying treatments.

5. Publications related to the thesis

Papers:

1. A. Paszternák, I. Felhősi, Z. Pászti, E. Kuzmann, A. Vértes, E. Kálmán: **„Surface analytical characterization of passive iron surface modified by alkyl-phosphonic acid layers”**, *Electrochimica Acta,* 55 (3), 2010, 804–812

2. A. Paszternák, S. Stichleutner, I. Felhősi, Z. Keresztes, F. Nagy, E. Kuzmann, A. Vértes, Z. Homonnay, G. Pető, E. Kálmán: „**Surface modification of passive iron by alkyl-phosphonic acid layers**”, *Electrochimica Acta*, 53 (2), 2007, 337-345

3. E. Kuzmann, S. Stichleutner, Z. Homonnay, A. Vértes, A. Paszternák, F. Nagy, I. Felhősi, G. Pető, J. Telegdi, E. Kálmán: **„Amorphous iron formation due to low energy heavy ion implantation in evaporated ^{57}Fe thin films”**, *Journal of Radioanalytical and Nuclear Chemistry*, 277, 2008, 699-702

4. A. Paszternák, A. Pilbáth, Z. Keresztes, I. Felhősi, J. Telegdi, E. Kálmán: „**Atomic force microscopy studies of alkyl-phosphonate SAMs on mica”,** *Materials Science Forum*, 589, 2008, 257-262

5. A. Paszternák, I. Felhősi, Z. Keresztes, E. Kálmán: **„Formation and structure of alkyl-phosphonic acid layers on passive iron”,** *Materials Science Forum*, 537-538, 2007, 239-246

Book chapters:

A. Csanády, E. Kálmán, G. Konczos (editors): **Bevezetés a nanoszerkezetű anyagok világába**, MTA Kémiai Kutatóközpont – Eötvös Kiadó, Budapest, 2009

III.2.3. chapter: E. Kálmán, I. Felhősi, A. Paszternák:

Önszerveződő rendszerek, page 96-100.

IV.1.7. chapter: E. Kálmán, P. M. Nagy, A. Paszternák:

Pásztázó tűszondás módszerek, page 172-182.

Conference proceedings:

A. Paszternák, I. Felhősi, Z. Pászti, E. Kuzmann, A. Vértes, J. Telegdi, E. Kálmán: “**Surface analytical characterization of alkyl-phosphonate thin layers on passive iron surface**”, *EUROCORR 2008, Proceedings on CD*

Oral presentations:

1. J. Telegdi*, L. Románszki, A. Paszternák, É. Pfeifer, T. Keszthelyi, E. Kuzmann, A. Vértes, E. Kálmán: „**Special hydrophobic nanocoatings for controlling corrosion and microbial adhesion**”, 7th International Symposium on Electrochemical Micro and Nano System Technology, 15-18th September 2008, Ein Gedi, Israel

2. A. Paszternák, I. Felhősi, Z. Pászti, E. Kuzmann, A. Vértes, J. Telegdi*, E. Kálmán: **„Surface analytical characterization of alkyl-phosphonate thin layers on passive iron surface"**, EUROCORR 2008, 7-11th September 2008, Edinburgh, UK

3. E. Kalman*, I. Felhosi, A. Paszternák**: "Passive iron surface modified by phosphorous derivative",** The International Conference on Technological Advances of Thin Films & Surface Coatings ("Thin Films 2006"), 11-15th December 2006, Singapore

4. A. Paszternák, S. Stichleutner, F. Nagy, I. Felhősi, E. Kuzmann, A. Vértes, Z. Keresztes, E. Kálmán*: "**Surface modification of passive iron by alkyl-phosphonic acid layers",** The 57th Annual Meeting of the International Society of Electrochemistry, 27th August – 1st September 2006, Edinburgh, UK

5. E. Kuzmann*, S. Stichleutner, Z. Homonnay, A. Vértes, K. Havancsák, C. Tosello, G. Principi, O. Doyle, C. Chisholm, M. El-Sharif, A. Paszternák, F. Nagy, I. Felhősi, E. Kálmán: „**Mössbauer investigations of amorphous iron formation due to heavy ion irradiation",** Sixth Workshop on Mössbauer Spectroscopy, 7-11th June 2006, Seeheim, Germany

6. A. Paszternák, I. Felhősi, Z. Keresztes, E. Kálmán*: "**Surface modification of passive iron by self-assembled monolayer",** The 56th Annual Meeting of the International Society of Electrochemistry, 26-30th September 2005, Busan, Korea

7. I. Felhősi, A. Paszternák, T. Rigó, Z. Keresztes, A. Pilbáth, J. Telegdi, E. Kálmán*: **"Interfacial studies on SAM and LB nanolayers of alkyl-phosphonate",** 29th International Conference on Solution Chemistry, 21-25th August 2005, Portorož, Slovenia

Oral presentations in Hungarian:

1. Paszternák András*, Szabó Imola, Keresztes Zsófia, Felhősi Ilona, Kálmán Erika: „**Monorétegek vizsgálata pásztázó tűszondás mikroszkóppal",** PhD hallgatók anyagtudományi napja VIII., 27th November 2008, Veszprém, Hungary

2. Paszternák András***,** Felhősi Ilona, Pászti Zoltán, Stichleutner Sándor, Kuzmann Ernő, Nagy Ferenc, Vértes Attila, Pető Gábor, Kálmán Erika**: „Funkcionális vékonyrétegek jellemzése felületvizsgálati- és felületanalitikai módszerekkel",** XI. Kémia Doktori Iskola, 21-22nd April 2008, Mátrafüred, Hungary

3. Paszternák András*, Stichleutner Sándor, Felhősi Ilona, Keresztes Zsófia, Pászti Zoltán, Kuzmann Ernő, Nagy Ferenc, Vértes Attila, Pető Gábor, Kálmán Erika: „**Korrózióvédő vékony szerves rétegek jellemzése felületanalitikai és felületvizsgálati módszerekkel”,** PhD hallgatók anyagtudományi napja VII., 28th November 2007, Veszprém, Hungary

4. Paszternák András*, Stichleutner Sándor, Felhősi Ilona, Keresztes Zsófia, Pászti Zoltán, Kuzmann Ernő, Nagy Ferenc, Vértes Attila, Pető Gábor, Kálmán Erika: „**Alkil-foszfonát korrózióvédő rétegének vizsgálata passzivált vas felületén”,** MTA KK Kutatóközponti Tudományos Napok, 23rd May 2007, Budapest, Hungary

Young Scientist Award at the Science Days of the Chemical Research Center of the Hungarian Academy of Sciences in 2007

5. Paszternák András*, Felhősi Ilona, Keresztes Zsófia, Nagy Péter, Kálmán Erika: „**A pásztázó tűszondás mikroszkópia alkalmazása önszerveződő molekulák rétegeivel módosított felületek vizsgálatára”,** X. Kémia Doktori Iskola, 7th May 2007, Mátraháza, Hungary

6. Paszternák András*, Stichleutner Sándor, Felhősi Ilona, Nagy Ferenc, Keresztes Zsófia, Kuzmann Ernő, Vértes Attila, Kálmán Erika: „**Passzivált vas felületének módosítása alkilfoszfonátokkal”**, PhD hallgatók anyagtudományi napja VI., 14th November 2006, Veszprém, Hungary

7. Felhősi Ilona*, Keresztes Zsófia, Telegdi Judit, Kármánné Herr Franciska, Pilbáth Aranka, Paszternák András, Kálmán Erika: „**Foszfonát vékonyrétegek kialakulása és korrozióvédő hatása vas felületen”**, MTA Elektrokémiai Munkabizottság, 22nd January 2007, Budapest, Hungary

8. Paszternák András*, Keresztes Zsófia, Nagy Péter, Felhősi Ilona, Kálmán Erika: „**Fémfelületek módosításának nyomonkövetése pásztázó tűszondás módszerekkel”**, MTA Elektrokémiai Munkabizottság, 22nd January 2007, Budapest Hungary

9. Paszternák András*: „**Funkcionális nanobevonatok – 3. féléves kutatási beszámoló”,** ELTE Kémia Doktori Iskola, Budapest, 11th November 2006, Budapest, Hungary

10. Paszternák András*, Felhősi Ilona, Keresztes Zsófia, Kálmán Erika: „**Foszfonát réteg képződési kinetikájának tanulmányozása atomi erőmikroszkóppal”**, IX. Kémia Doktori Iskola, 24-25th April, Tahi, Hungary

11. Paszternák András*, Felhősi Ilona, Keresztes Zsófia, Kálmán Erika: „**Szerves védőréteg kialakulásának és szerkezetének tanulmányozása passzivált vas felületen**”, PhD hallgatók anyagtudományi napja V., 21st November, Veszprém, Hungary

12. Paszternák András*, Felhősi Ilona, Keresztes Zsófia, Kálmán Erika: „**Alkil-foszfonát réteg kialakulásának és szerkezetének tanulmányozása passzivált vas felületen”,** V. Országos Anyagtudományi Anyagvizsgálati és Anyaginformatikai Konferencia és Kiállítás, 9-11th October 2005, Balatonfüred, Hungary

13. Paszternák András*, Felhősi Ilona, Keresztes Zsófia, Kálmán Erika: „**Szerves vegyületek adszorpciója passzivált vas felületen**”, VIII. Kémia Doktori Iskola, 5-6th May 2005,Tahi, Hungary

Posters:

1. A. Paszternák*, I. Felhősi, Z. Keresztes, E. Kálmán: „**Atomic force microscopy studies of alkyl-phosphonic acid layers on different substrate”,** Seeing at the Nanoscale VI, 9-11th July 2008, Berlin, Germany

2.. A. Paszternák*, A. Pilbáth, Z. Keresztes, I. Felhősi, J. Telegdi, E. Kálmán: „**Atomic force microscopy studies of alkyl-phosphonate SAMs on mica”,** 6th Hungarian Conference on Materials Science, 14-16th October 2007, Siófok, Hungary
Poster Award of the Scientific Board - 6th Hungarian Conference and Exhibition on Materials Science Testing and Informatics, Siófok, Hungary, 2007

3. A. Paszternák*, Z. Pászti, I. Felhősi, E. Kálmán: „**Passive iron surface modified by Alkyl-Phosphonate SAMs”,** HUNN – Hungarian Network of Excellent Centers of Nanosciences, 2nd Transfer Day, 11th October, Budapest, Hungary

4. A. Paszternák*, Z. Pászti, I. Felhősi, E. Kálmán: „**Passive iron surface modified by alkyl-phosphonate SAMs**”, 12th European Conference on Applications of Surface and Interface Analysis, 9-14th September 2007, Brussels, Belgium

5. A. Paszternák*, I. Felhősi, Zs. Keresztes, E. Kálmán: „**Alkyl-phosphonic acid layer formation on passive iron surface”,** 6th International Symposium on Electrochemical Micro and Nano System Technology, 22-25th August 2006, Bonn, Germany

6. A. Paszternák*, Z. Keresztes, I. Felhősi, A. Pilbáth, E. Kálmán: „**Formation and structure of self-assembled monolayers of alkyl-phosphonate on mica”,** Nano-Chemistry Workshop of COST Chemistry Action D19 “Chemical Functionality Specific to the Nanometer Scale”, Koç University, 1-4th September 2005, Istanbul, Turkey