

Corrosion in Power Industry



Edited by
Maroš Halama and Jan Stoulik

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Jan Stouilil

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Special topic volume with invited peer reviewed papers only.

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Preface

Nowadays trend in application of eco policy, more strict legislative and globalisation in economy together with research and development in emerging technologies such as nanotechnology bringing also new corrosion challenges into the power industry sector. New alloys and composite materials, eco-friendly energy systems, effective monitoring techniques and sophisticated prediction methods contribute on safer and more reliable operation of energy units. All up-mentioned circumstances required interdisciplinary approach to build perspective solutions with aim to minimize degradation process of components made from different materials used in power industry. In this special issue you can find papers dealing with application of nanotechnologies, corrosion monitoring techniques, materials characterisation but also several case studies from corrosion failures in power industry. All these information contribute on expansion of knowledge database, which is highly sufficient in the area with main aim to prevent against corrosion failures.

Collective of authors: Editors & Maria Hagarova

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I. Degradation of Solar Cells

Non-destructive technique for evaluation of degradation on solar cells

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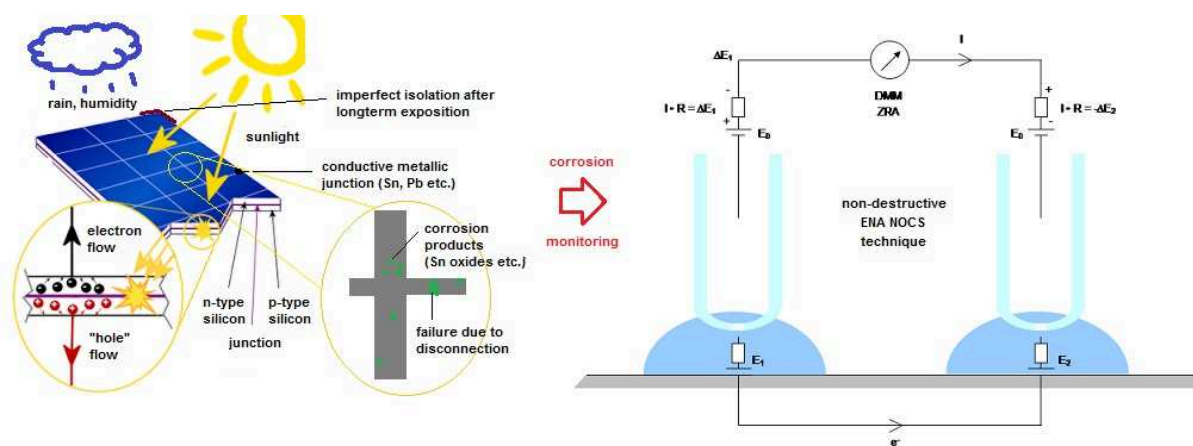
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Keywords: corrosion, solar energy, electrochemical noise, ENA

Abstract:

Corrosion is one of the most decisive factors determining the lifetime of materials, especially of the surface layers. Monitoring corrosion rate and mapping the overall corrosion on the surface of solar cells become very important step in preventing failures in long-term atmospheric exposure. Electrochemical noise technique in no contact to the substrate setup (ENA NOCS) as non-destructive technique was used to monitor potential and current and finally calculation of noise resistance ratio R_n was determined. The technique is already successfully executed on zinc and zinc alloy coatings [1] and organic coatings [2]. In this paper, the reliability of the corrosion monitoring system in adapting the technique to measure potential and current fluctuations on silicon based photovoltaic solar cells was verified. Tests were performed and finally compared on monocrystalline and polycrystalline silicon using different approaches (placement of sensor, intensity of light etc.)

Graphical abstract:



Non-destructive corrosion monitoring on solar cells

1. Introduction

Solar technology is among the fastest growing sectors and has become a very important field of research in this century. A lot of different types of solar panels have been developed through the years. Next to price, availability and toxicity of resources, difficulty of the manufacturing process, the efficiency of the solar cell is also a very important property. Direct conversion of sunlight into electricity and heat is carried out on thin films of high purity materials equipped with suitable physical properties. These materials are very sensitive to external operational factors that cause degradation of optical, chemical and electrical properties. Gradual degradation of photovoltaic cells can be caused by solar radiation – e.g. LID, „light induced degradation“, chemical and

electrochemical degradation- e.g. snail trails, cell cracks or delamination, cleaning or pollution and thermal degradation, e.g. occurrence of hot spots. Corrosion on the surface of a solar cell may influence the overall efficacy [3]. Corrosion is one of the decisive factors influencing the lifetime of metallic materials, especially of surface layer due to the interaction with environment via humidity, presence of contaminants, ultraviolet radiation etc. Failure of materials should be prevented in case of solar cells under wide spectrum of atmospheric conditions and thus detection of quality of surface is very important. All types of degradation of solar photovoltaic cells modules are combined with each other and could cause permanent damage [4].

Most types of failures are caused by physical mechanism, such as fatigue, disconnection of wire contacts, junctions, welds etc. Here, corrosion play such an important support role.

Nowadays, trend in research and development in various kind of industry is to implement non-destructive technique for monitoring of quality of coating materials or corrosion activity/passivity.

A rather new, but very reliable method to measure the corrosion activity, mechanism of corrosion is electrochemical noise in special arrangement. One of the hybrid of ENA technique fulfilling criteria is electrochemical noise analysis (ENA) in no contact to the substrate setup (NOCS). The advantage of this type of electrochemical noise is that can be measured in freely corroding system. Previously, this method is already used to investigate the corrosion rate on zinc coatings and organic coating used in automotive industry [1,5]. The NOCS monitors potential and current in specific setup, using quasi sensor, where two electrodes are connected to a source and to the sample via special electrolyte [1]. By calculating the standard deviation of the measured potential and current, the noise resistance ratio R_n can be determined. This ratio gives an idea of the corrosion rate present on the conductive or nonconductive sample or quality of coatings on selected metallic surface.

Atmospheric corrosion modelling

Atmospheric corrosion can be attributed to three factors. First type is the influence of the atmosphere via humidity, temperature, pH, contaminants. There is also considerable influence of the surface material, its structure, chemical composition, solubility, hygroscopic properties and corrosion layer changes during exposition. The last parameter is the way the object is exposed such as shielding, radiance, time of exposure etc. All these influences on the corrosion rate can be modelled using artificial neural network (ANN). Here, historical data from previous corrosion measurements and atmospheric parameters are implemented in huge database and trained to predict mass losses of metallic materials [6]. One of the output can be interpreted using 2D maps.

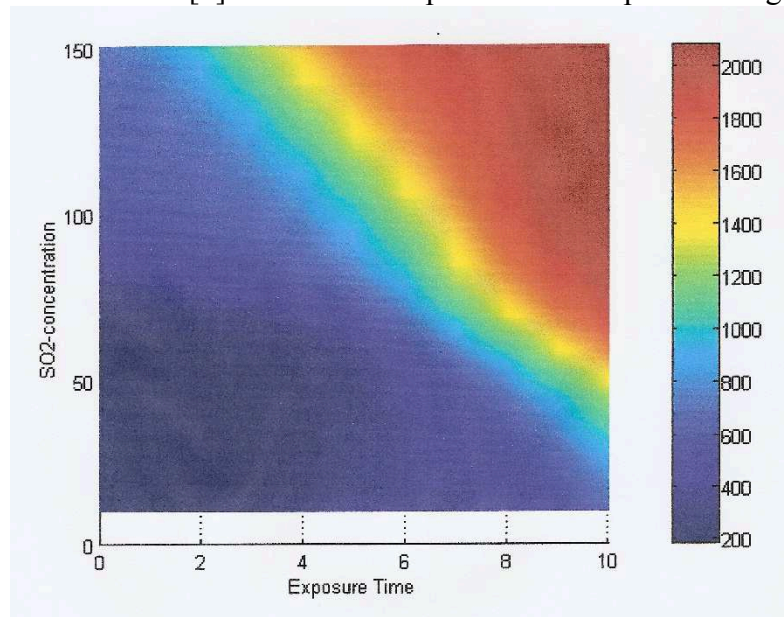


Fig.1 The 2D colour map of predicted corrosion mass loss $[g.m^{-2}]$ for metallic material (steel) during 10 years period in whole concentration range of SO_2 $[\mu g.m^{-3}]$ as contaminant [6].

Corrosion monitoring

There exist a wide variety of methods to monitor the corrosion resistance of coatings on metals. Traditionally, coated metal plates were subjected to a cabinet test under special conditions (humidity, light intensity, salt etc.) to simulate exposition in short time. Evaluation of the occurred corrosion can be carried out e.g. by visual inspection and comparison with standard samples. To avoid of errors coming from subjective evaluation, one of approach is application of electrochemical approaches by measuring of corrosion resistance etc. Mansfeld et. al. used electrochemical impedance spectroscopy (EIS) and electrochemical noise analysis (ENA) for non-destructive evaluation of corrosion processes. He determined relationship between the polarization resistance R_p obtained from EIS data and the noise resistance R_n determined by statistical analysis of potential and current noise data. ENA technique offer accurate, sensitive, robust, versatile and very fast results [7].

Electrochemical noise

One of the numerous electrochemical techniques to analyze corrosion behavior of coatings is Electrochemical Noise Analysis (ENA) in NOCS setup as non-destructive technique using 3-electrodes, of which one is working electrode and two are reference electrodes. By measuring the current between the two working electrodes at regular intervals, the potential and current data are obtained. The parameter representing the corrosion resistance is the noise resistance R_n , which is calculated as [2]:

$$R_n = \frac{Stdev E}{Stdev I}$$

Where $Stdev E$ is the standard deviation of the potential and $Stdev I$ the standard deviation of the current.

Next to the noise resistance, the technique also allows computation of the pitting index ratio. The pitting index ratio is calculated as:

$$PI = \frac{Stdev I}{RMS I}$$

where $RMS I$ is the root mean square value of the measured current i . By this pitting index ratio, the type of corrosion that is present on the sample can be determined [7].

Experimental

For measurements of electrical noise, an experimental setup was developed (Fig.2). Two electrodes are placed on the top of the sample in the sample holder filled with SARS solutions (0.01 M HNO_3 , 0.001M $NaCl$ and 0.001M $(NH_4)_2SO_4$). These electrodes are connected to a source and whole set-up is protected against fluctuations from environment by a Faraday cage.

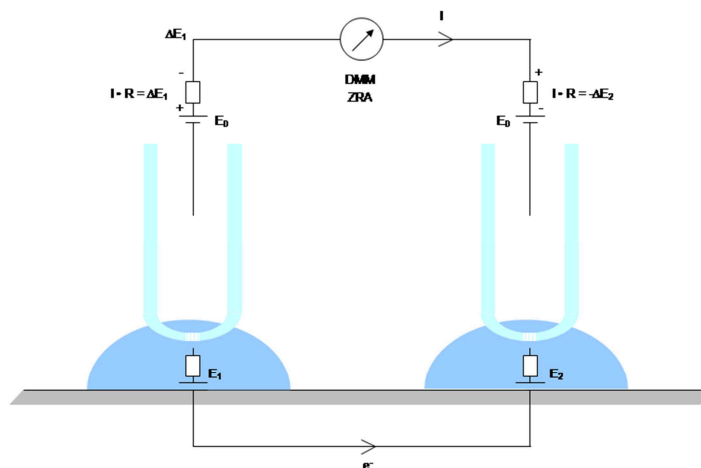


Fig. 1 Schematic representation of electric setup of NOCS ENA [1]

Measurements of potential and current were realized separately in 2 minutes monitoring. For current measurements a resistance of 1 or 100 MOhms is added in the circuit, dependent on the order of magnitude of the current values. The measured data are processed in programme NoiseJazz2012 for statistical evaluation and visualization of corrosion activity/passivity [1].

The technique was already successfully executed on zinc coatings and organic coatings on zinc. Here, the new challenge is to adapt the technique to measure potential and current fluctuations on silicon based solar cells. Due to the fact that corrosion rate is influenced by several factors such as humidity, light intensity, temperature, concentration of pollutants etc., tests were executed on polycrystalline sample at different light intensities. The blackbox measurement tends to have higher corrosion resistance compared to measurements at increased light conditions.

Experimental

Scanning electron microscopy

Set of two series of samples were used, all composed of mainly silicon with thin metallic lines for transport of the electrons. These thin lines are mutually connected by thicker metallic strips. The SEM-images of the monocrystalline silicon-based solar panel are shown in Fig.2. Samples were detected by Scanning Electron Microscopy (SEM) and chemical analysis of the different parts were examined using Energy-Dispersive X-ray spectroscopy (EDX).

An EDX analysis shows the chemical composition of specific parts of the sample. An overview of the different spectra of the metallic parts is depicted in Fig.2a. In Figure 2b, the chemical composition of the thick metal strip is shown. Next to a majority of tin, the metal band also contains presence of lead and oxygen. For the thin band, the chemical composition is similar.

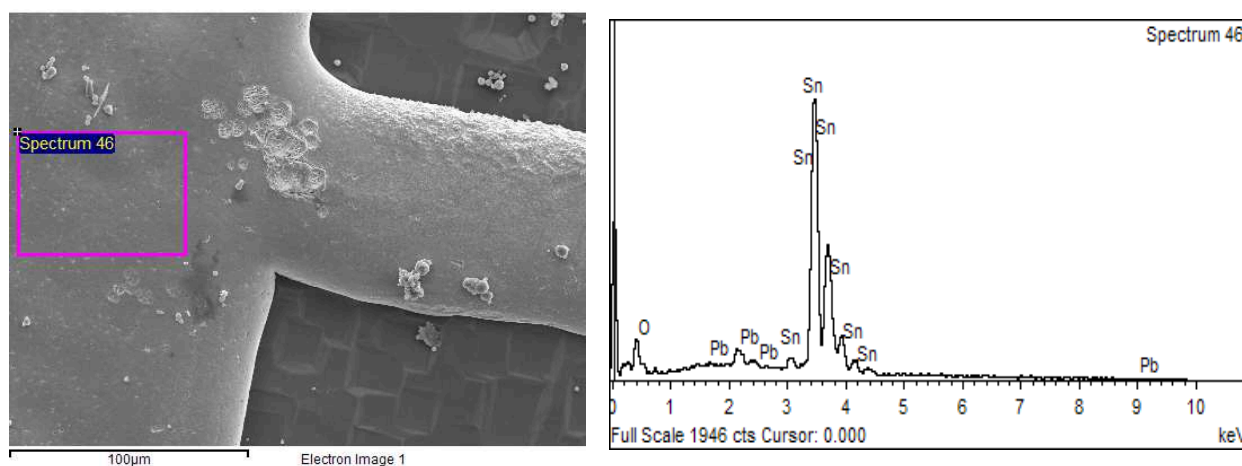


Fig.2a) SEM-image and 2b) EDX analysis of the boundary metallic part/monocrystalline silicon based solar panel

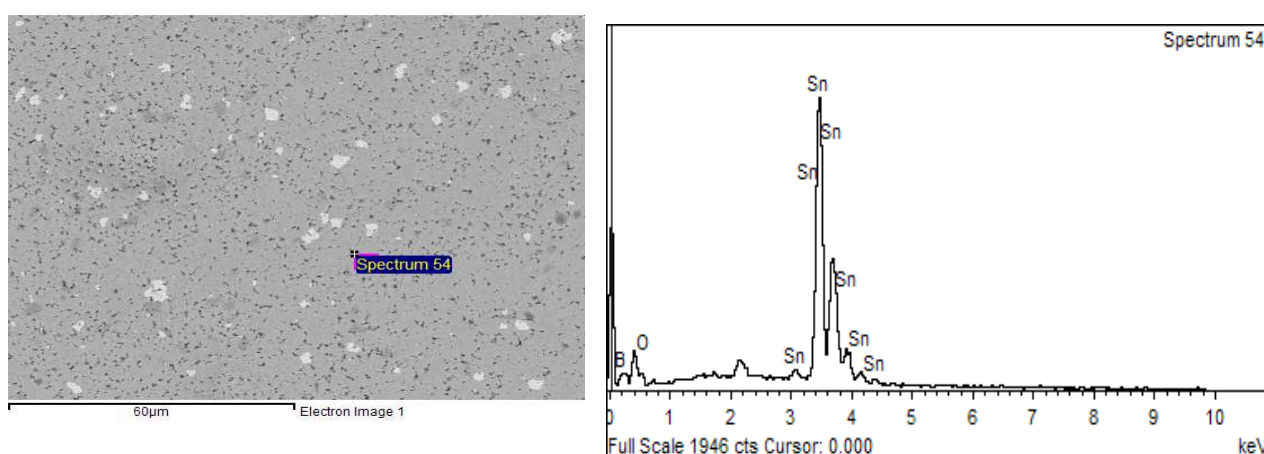


Fig.3a) SEM-image (COMPO regime) and 3b) EDX analysis of the metallic part of monocrystalline silicon based solar panel

Fig.3a shows external surface of the metallic strips of the sample prior to the immersion in measuring solution. It clearly seen that precipitates with a different chemical composition were found. Their chemical composition consist mainly of Sn and O, but also around 1.4% of B was detected.

Electrochemical noise

The noise measurements have been carried out at ambient temperature and using low concentration chloride containing aqueous electrolytes. The basis of measuring system was digital multimeter Keithley 2100 connected via LPHM07 unit and a personal computer. Resolution of the system was 1nA for current and 1µV for voltage measurements. The sampling rate was 10 Hz and in one test 2000 values were collected.

After noise measurement, the data were processed using Matlab. The data of potential (after 20 minutes) for the monocrystalline and polycrystalline material are shown in Figure 4a,b. The parallel position of the electrodes clearly formed more fluctuations in the potential. The monocrystalline material also reaches higher values for the fluctuations.

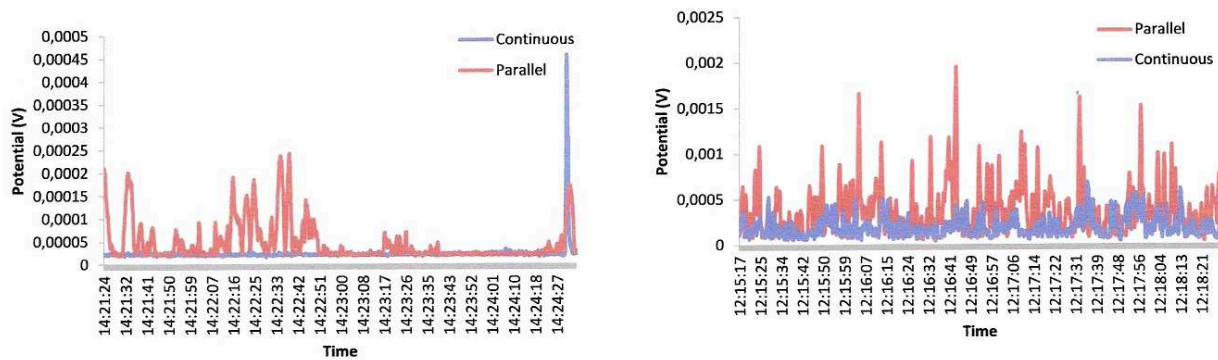


Figure 4 Values of potential noise after 20 minutes for a) monocrystalline and b) polycrystalline silicon solar cell (parallel vs. continuous direction).

The current fluctuations of the monocrystalline and the polycrystalline silicon in parallel and continuous position of the electrodes are shown in Figure 5a,b. In the monocrystalline material, the fluctuations and values for the current for continuous and parallel are more or less the same. In the polycrystalline material however there is a clear difference. The fluctuations for the continuous case were much smaller. This occurs due to the fact that there is an easy conducting way through the metal band in the continuous set-up, so the electrons don't have barrier in silicon material.

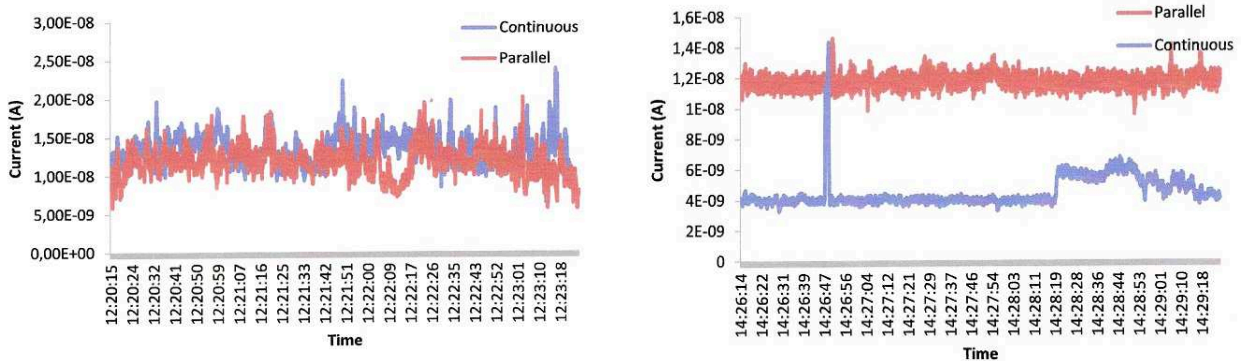


Figure 5 Values of current noise after 20 minutes for a) monocrystalline and b) polycrystalline silicon solar cell (parallel vs. continuous).

The values for $Stdev E$, $Stdev I$ and Rn are given in Table 1. The largest noise resistance is found for the monocrystalline solar cell, and this in the parallel position. The parallel set-up is the better indicator for the corrosion rate of the silicon material, evidenced by the comparable values for the three solar cell in continuous position. The multicrystalline and polycrystalline give a lower noise resistance ratio for parallel than the monocrystalline, indicating a higher corrosion activity. Some preliminary measurements and analysis of ENA monitoring indicate that from Rn values detection can not only reveal corrosion activity, but in certain extent efficacy in charge transfer process is possible to assess.

Table 1 Standard deviations for potential and current vs. calculation of noise resistance ratio for mono and polysilicon solar cell in parallel and continuous set-up.

Sample / Position	Stdev E [V]	Stdev I [A]	Rn [Ohm]
Mono / Parallel	3.79E-04	1.20E-08	31 660
Mono / Continuous	1.34E-04	1.30E-08	14 832
Poly / Parallel	4.59E-05	1.17E-08	3 904
Poly / Continuous	2.41E-05	4.47E-09	5 383

Conclusions:

A corrosion monitoring system based on no contact to the substrate setup of electrochemical noise analysis tested on the surface of silicon solar cells in pilot experiments showed big influence of light intensity on detection of corrosion activity on metallic components made of Pb and Sn. However, there is a need to look at other practical consideration of making non-destructive ENA measurements suitable for assessment of efficacy of charge transfer during long-term exposition.

Due to the fact that there is an easy conducting way through the metal band in the continuous set-up in placement of corrosion monitoring sensor and electrons don't have barrier in silicon material, the continuous set-up is not very suitable for correct representation of corrosion activity.

There is a big potential to observe problematic parts of photovoltaic cells caused by chemical and electrochemical degradation by corrosion monitoring technique, all before visual inspection get results.

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References:

- [1] Halama, M., Zhu Y., Koval', K., Brezinová, J.: Quantification of corrosion activity on HDG steel sheets during cyclic dip tests in classical and ecological salt solutions, In: Acta Metallurgica Slovaca, Vol. 20 (2014) pp. 89-96
- [2] Mabbut, S., Mills, D.J., Woodcock, C.P.: Developments of the electrochemical noise method for more practical assessment of anti-corrosion coatings, In: Progress in Organic Coatings, Vol. 59 (2007)
- [3] Monbaliou, O.: Application of NOCS for corrosion measurement on solar cells, Internship report from IAESTE stage at TUKE, 2013
- [4] <http://www.photovoltaikebuero.de> [cited 29.07.2014]

- [5] Halama, M. et. al.: Active corrosion management in automotive industry: hyphenation of electrochemical noise analysis with artificial neural networks – feasibility study, EUROCORR 2009 – The European Corrosion congress, 6.-10.9.2009, Nice
- [6] Halama, M., Kreislova, K., Lysebettens, J. V.: Prediction of Atmospheric Corrosion of Carbon Steel Using Artificial Neural Network Model in Local Geographical Regions, In: Corrosion: The Journal of Science and Engineering, Vol. 67, no. 6 (2011), p. 1-6, ISSN 0010-9312
- [7] Mansfeld, F., Xiao, H., Wang, Y.: The use of electrochemical impedance spectroscopy (EIS) and electrochemical noise analysis (ENA) for monitoring of biocorrosion, In: Conference proceedings: Tri-service conference on corrosion, Orlando, Florida, 1994

Effect of Humidity on Selective Surface of Solar Absorber Plates

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Keywords: selective surface, periodic reverse current, humidity, IR spectroscopy.

Abstract: Selective layers Al₂O₃-Ni were prepared by electrochemical way applying anodic oxidation of aluminium and electrolytical colouring. Anodic oxidation of aluminium was realised in sulphuric resp. phosphoric acid and colouring was carried out under periodic reverse current using different colouring electrolytes on nickel basis. The selective layers were studied and analysed with diverse methods before and after exposition to humidity effect. A way of the selective layer preparation is decisive to the final reaction with humidity and so to degradation of the material.

Introduction

Solar energy could be one of primary sources of energy because it is ecologically clean and is freely available to everyone over the long time periods. The most common use of solar energy includes its transformation in either thermal energy by means of thermal collectors or in electrical energy by means of photovoltaic collectors. Thermal collectors can be used for heating the sanitary water in private houses, blocks of flats, tourists' objects, hospitals, schools or other buildings. Solar energy must be captured and converted. Solar collectors absorb the incident solar radiation, convert it into heat and transfer this heat to a coolant flowing through the collector. Flat plate solar collector consists of an absorber (Cu or Al) and a glazing, separated by an air layer. Optimization of solar heating system ensures maximal collected heat. Main parameters to be considered are related with both geometry and materials properties. There are three transfer modes: optical, radiative and convective. To maximize the energy collection the absorber of a collector should have a coating that has high absorptance for solar radiation (short wavelength) and low emittance for re-radiation (long wavelength). Such a surface is referred to as a selective surface. The absorptance of the collector surface for shortwave solar radiation depends on the nature and colour of the coating and on the incident angle [1].

Absorber of the classical flat collector on aluminium basis is the focus of our study. Up to now the selective layer Al₂O₃-Ni of the absorber is produced by two step electrochemical process. The process consists of anodic oxidation of the substrate in phosphoric acid electrolyte under direct current and electrochemical deposition of nickel under alternating current in colouring electrolyte on nickel basis with complexing agent sulfo- isophthalic acid (SIF). The selective layer Al₂O₃-Ni was formed employing in the second step for nickel electrodeposition periodic reverse current with an alternative of applying colouring electrolytes without complexing agents. The advantage of periodic reverse current is precise process parameter tailoring to prepare the layer/coating of requested quality [2]. The panels prepared in anodizing electrolyte sulphuric acid were prepared as well. The absorbers were afterwards exposed to humidity to study the selective layers quality.

Experimental methods

Aluminium finishes (Al 99.5%) with dimensions (3 x 8 x 0.1) cm were degreased in Aktigal 20 gdm⁻³ (MAG Slovakia), etched in a solution containing 50 g dm⁻³ of sodium hydroxide (Mikrochem, Slovakia) and immersed in 400 g dm⁻³ nitric acid (Mikrochem, Slovakia). All pre-

treatment operations were realized at 70 °C for 3 min. After each operation step a rinsing followed. Anodic oxidation was carried out in sulphuric acid and phosphoric acid electrolytes, respectively. The sulphuric acid electrolyte (180 g dm⁻³; Mikrochem, Slovakia) was applied at a current density of 1.5 A dm⁻², temperature 20 ± 2 °C with cooling and agitation for 40 min. An aluminium oxide (alumina) coating was formed after this operation. The rinsing of the finishes for 30 min followed to wash out the residual sulphate ions from the formed film. Alumina coating was prepared applying the phosphoric acid electrolyte as well (180 g dm⁻³; Lachema, Czech Republic) a current density of 0.35 A dm⁻², temperature 20 ± 2 °C with cooling and agitation for 20 min. The finishes were coloured by periodic reverse current (PRC). PRC colouring control was realised by the power supply (pe86c plating electronic Germany) with a rectangular wave at frequencies 30 Hz and 50 Hz with the areas of anodic and cathodic cycle keeping constant. Variable parameters of the process were the values of peak anodic and cathodic current, time of cathodic and anodic cycles and off time. The applied colouring electrolytes were used with (SIF and C marked colouring electrolytes) and without (S and W marked colouring electrolytes) complexing agents. All chemicals used have been of analytical grade.

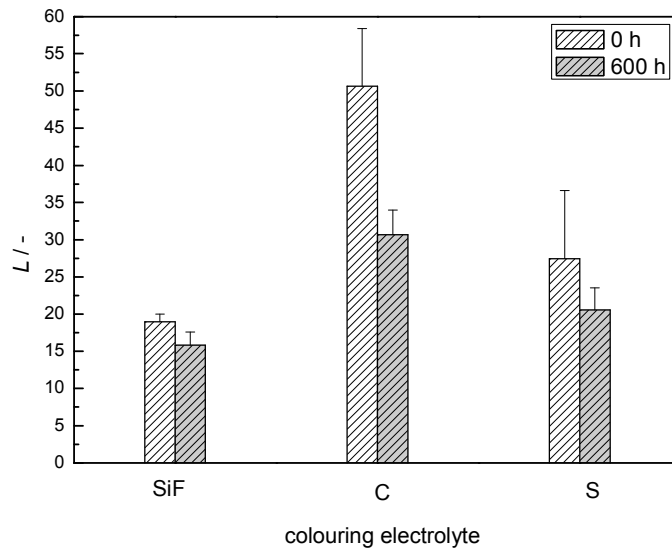
After colouring the parameters L^*a^*b of the colour space were measured by spectrophotometer Spectrodense A 504009 Premium (Techkon, Germany). The calibration was done against the white standard. The condensation tests were performed in a condensation chamber (ZKO 1 Kovofiniš, Czech Republic) at temperature (35±2) °C. The relative humidity was constant (98±2) %. Three samples from each parameters series were tested simultaneously. The samples were insulated and tilted at an angle of 45 ° to the horizon. The samples were exposed to humidity for up to 600 hours. IR spectra (FTIR Spectrometer Nicolet 5700, England) were collected after 80, 150, 300 and 600 hours exposition time to study the degradation of the prepared Al₂O₃-Ni selective layers on aluminium substrate. AC impedance measurements were realised in an unstirred aerated 3.5 wt. % potassium sulphate solution at ambient temperature. The EIS measurements of the prepared selective layers were performed by Autolab with FRA software and evaluated by ZsimWin 3.21 software. The as-deposited samples were immersed in the test solution for 10 min prior to this testing and before the measurements observe zero current potential (ZCP). An argento-chloride electrode (AgClE) and graphite were used as reference and counter electrodes, respectively. After humidity attack after 600 hours of exposition the ZCP and EIS measurements were carried out just for chosen samples treated in the sulphuric acid electrolyte for anodic oxidation.

Afterwards, aluminium oxide formed by anodic oxidation was stripped in chrome-phosphorous acid at 80 °C for 10 min. Chrome phosphorous acid 35 cm³ of phosphoric acid (Metrochem, Slovakia) and chromium oxide (VI) (Lachema, Czech Republic) 20 g dm⁻³ was replaced after 20 dm⁻² of the stripped area. Subsequently, the morphology, nickel content and distribution were studied by SEM, EDX and GDEOS analysis on the stripped finishes. The specimens' morphology was analysed by scanning electron microscope Zeiss EVO 40 (Zeiss, Germany) at an acceleration voltage of 20 kV. Nickel content was realised by EDX measurements JEOL JXA – 840A (Japan) and nickel distribution on the surface by GDEOS measurements LECCO 2000 (USA).

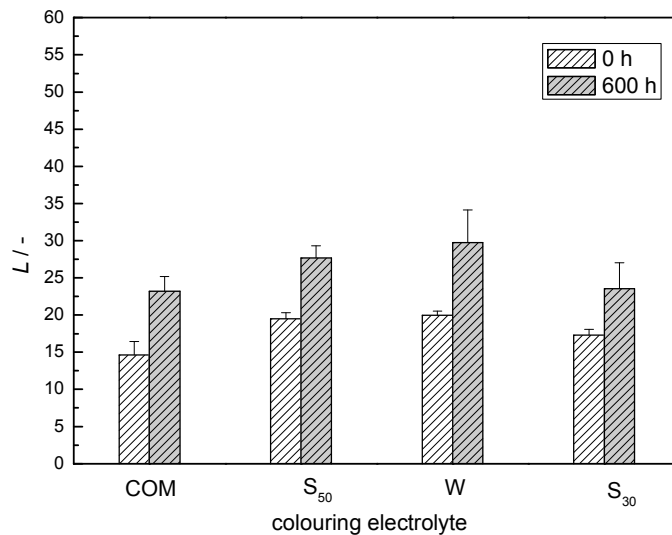
Results and discussion

Selective layers Al₂O₃-Ni were prepared by two-step process. Firstly by anodic oxidation of aluminium in the sulphuric respectively phosphoric acid electrolytes a porous layer of anodic aluminium oxide was formed. Then the layer was coloured applying periodic reverse current and diverse colouring electrolytes on nickel basis. Nickel was electrodeposited in the pores of anodic alumina to reach required colour of the absorber plate. Coloured finishes were evaluated by *spectrophotometry* with L^*a^*b parameters. The parameters characterize any colour by a luminance

parameter L and two colour coordinates a , b which specify the point on the chromaticity diagram [3]. Parameter L represents the colour shade of the finishes and parameters a , b characterize the brightness of the finishes. The parameters of the ideal black body represent values 0^*0^*0 . The L parameter is decisive for the coating quality at the tested conditions and results are summarized in Fig. 1.



a)



b)

Fig 1 Values of parameter L for different specimens in dependence on diverse colouring electrolytes for the selective layers anodized in a) sulphuric acid, b) phosphoric acid electrolyte

Fig. 1a) illustrates dependence of L values on colouring electrolyte for the finishes treated for anodic oxidation in sulphuric acid electrolyte. The values are recorded for as-deposited samples and after 600 hrs of humidity exposition. One can see the lowest value of parameter L was reached for samples coloured in the SiF colouring electrolyte. The quality of the selective layer coloured in C electrolyte type was not sufficient enough. All the tested coloured finishes indicate a drop of L value after 600 hrs humidity exposition. Fig. 1b) shows dependence of L values on colouring

electrolyte for the finishes treated for anodic oxidation in phosphoric acid electrolyte. Applying PRC there has been no option to colour the anodized substrate with the electrolytes containing complexing agent. The colouring electrolytes marked S and W were used, so the S colouring electrolyte was used applying two different frequencies (30 Hz and 50 Hz). Luminance parameter L of the commercial absorber reaches the value 14. It is clearly seen that values of parameter L for the prepared Al_2O_3 -Ni selective layers are comparable for all studied colouring electrolytes. After 600 hrs of humidity exposition the values of parameter L of all analysed specimens are growing. The results indicate the fitting values are obtained for the finishes treated in phosphoric acid especially in colouring electrolyte marked S applying frequency of PRC 30 Hz. Comparable values of parameter L are reached for finishes treated for anodic oxidation in sulphuric acid electrolyte and coloured in SIF electrolyte. Different behaviour of the specimens after humidity attack will be discussed later and is connected to the pores type formed after anodic oxidation.

Fig. 2 shows a relation between parameter L and nickel content. Lower nickel content in the selective layer has an impact on higher values of the L parameter. The lowest nickel content was found in the selective layer based on C colouring electrolyte type 7 at %, the highest amount was found in selective layer with SIF colouring electrolyte 26 at %. Values of parameter L are corresponding to the values (51 and 19).

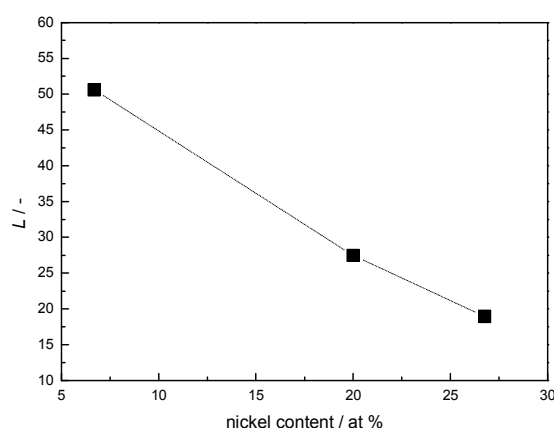


Fig 2 Dependence of parameter L values on nickel content for the specimens anodized in sulphuric acid electrolyte

Morphology of nickel on aluminium substrate after anodic alumina stripping is shown in Fig. 3. The finishes were analysed as deposited and after humidity exposition applying stripping procedure - dissolution of anodic alumina layer in chrome-phosphoric acid. There is a difference in nickel arrangement due to the pattern of pores formed by anodic oxidation in the diverse types of anodizing electrolytes. There are nickel fibres, heterogeneously arranged, spatial (Fig. 3a) and nickel nods, homogeneously arranged on the surface of the aluminium substrate (Fig. 3b). The first ones are formed in the pores of anodic alumina in sulphuric acid electrolytes, the second ones in phosphoric acid electrolytes.

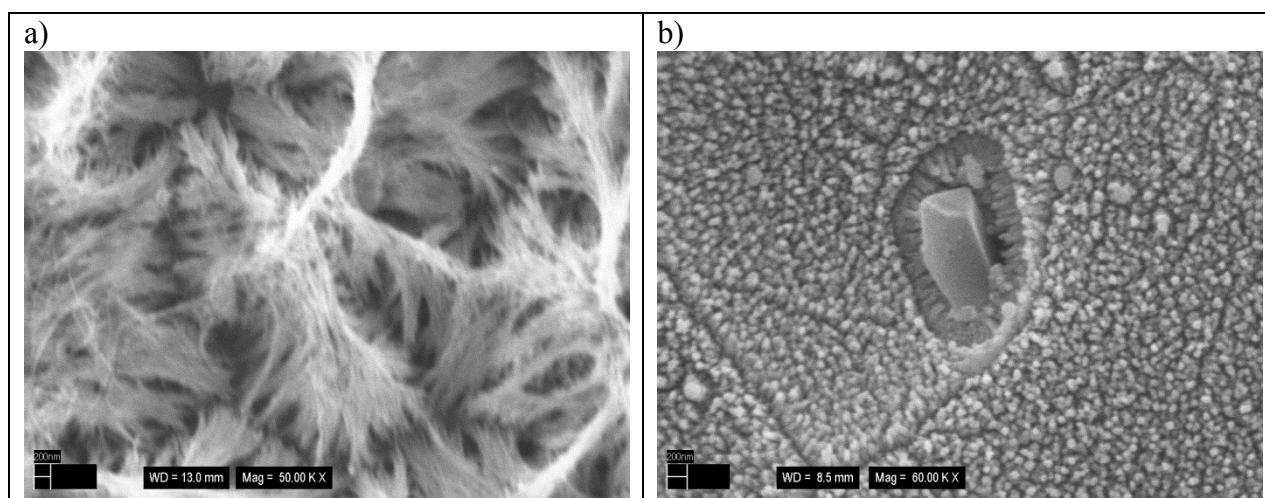


Fig 3 Morphology of nickel on aluminium substrate after stripping of anodic Al_2O_3 prepared in a) sulphuric acid, b) phosphoric acid electrolyte

Depth profiles were recorded after stripping of anodic alumina as well. The measurements were realised for as deposited and exposed specimens. In general, *GDOES* measurements confirmed for all studied finishes a presence of nickel on the substrate surface regardless of anodizing electrolyte, colouring electrolyte, as-deposited specimens and the exposed specimens (Fig. 4).

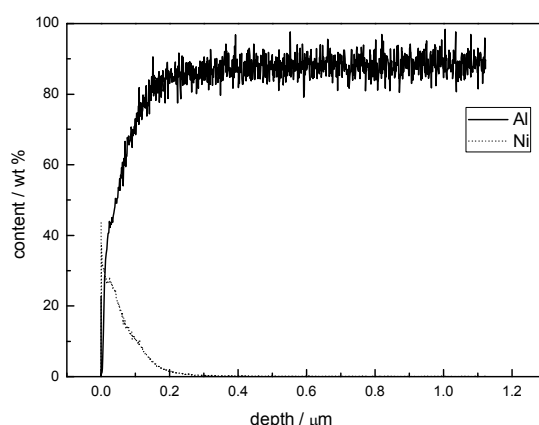
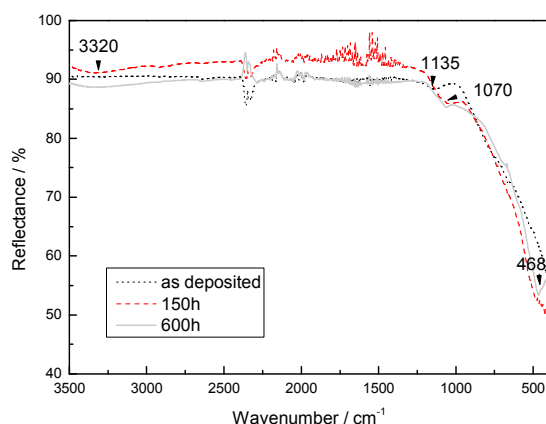


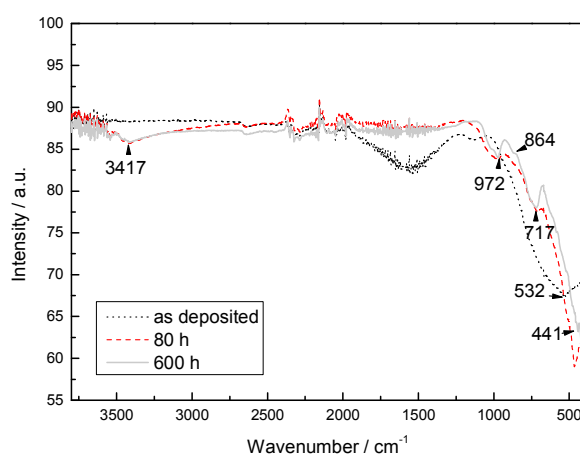
Fig 4 GDEOS record of the selective layer specimens

Infrared spectroscopy was performed over the range $400\text{--}4000\text{cm}^{-1}$ (Fig. 5). ATR (Attenuated Total Reflectance) technique was used for collecting data. Identification of IR spectra was made after chosen exposition time (0, 80, 150, 300 and 600 h) to study humidity effect on the absorber plate. Fig. 5a) shows spectra of the tested samples after 0, 150 and 600 h exposition time applying sulphuric acid as oxidizing electrolyte. Absorption bands at 1064 cm^{-1} and 471 cm^{-1} correspond to boehmite $\text{AlO}(\text{OH})$ [4]. In the range of $3000\text{--}3500\text{ cm}^{-1}$ OH vibrations were identified representing the presence of bound water in the coating. Generally, the degradation process of the samples is comparable for these types of the specimens. The vibration bands of boehmite and OH groups were analysed for samples coloured by PRC in C electrolyte already after 150 h of exposition time. The vibration bands for the rest of analysed samples appeared after 300 h exposition time. Fig. 5b) shows reflectance spectra of the coloured and exploited films applying phosphoric acid anodizing electrolyte after 0, 80 and 600 h exposition time. The coloured film has a reflectance between ~ 90 and $\sim 70\%$ and the exploited films between ~ 90 and $\sim 60\%$. $\text{Ni}(\text{OH})_2$ was identified through strong

bands at 440, 540, 725, 975 and 3640 cm^{-1} and weak ones at 830 and 864 cm^{-1} . The sharp spike at 3640 is not observed however the broad band at 3417 cm^{-1} appeared. Some authors observed bands around 332, 530 and 3636 cm^{-1} [5]. Band centred around 440 cm^{-1} is controversial since it can be assigned as translational or rotational lattice mode [5]. The broad signal about $\sim 3400\text{ cm}^{-1}$ is characteristic of bound OH groups and water and broad signal is due to lattice water incorporated in the porous film [6]. One can conclude that a structure of the coloured film reacting with humidity consists of Ni intercalated with water through H bonds and on the surface is adsorbed water as well. Similar structure was observed in [7].



a)



b)

Fig 5 IR reflectance spectra of the finishes oxidized in a) sulphuric acid, b) phosphoric acid electrolyte

Zero Current Potential (ZCP) measurements show dependence on nickel amount for the analysed finishes (Fig. 6). The specimens were prepared with different colouring electrolytes on anodic oxidized aluminium substrate in the sulphuric acid electrolyte. As discussed/mentioned above the lowest nickel content has been in selective layer electrodeposited with C colouring electrolyte 7 at %, the highest amount was found in selective layer with SIF colouring electrolyte 26 at %. There is a linear dependence on nickel in the selective layer and ZCP. ZCP reached the highest value (-0.34 V) for the samples with minimum nickel and vice versa the lowest one with maximum nickel content in the selective layer (-0.54 V). After 600h following hydration a reverse effect concerning the dependence of ZCP on nickel content appeared. This effect could be explained in a following

way. The samples as deposited consist of Al_2O_3 layer and Ni at the bottom of the pores. The Al_2O_3 layer is in fact passive layer, so low nickel amount allows prevailing Al_2O_3 shift potential to higher values. On the other hand after hydration new hydroxide-oxide forms appeared and water molecules are inbuilt in the pores of anodic alumina as well as it is confirmed by IR measurements. These effects have shifted ZCP to reverse values.

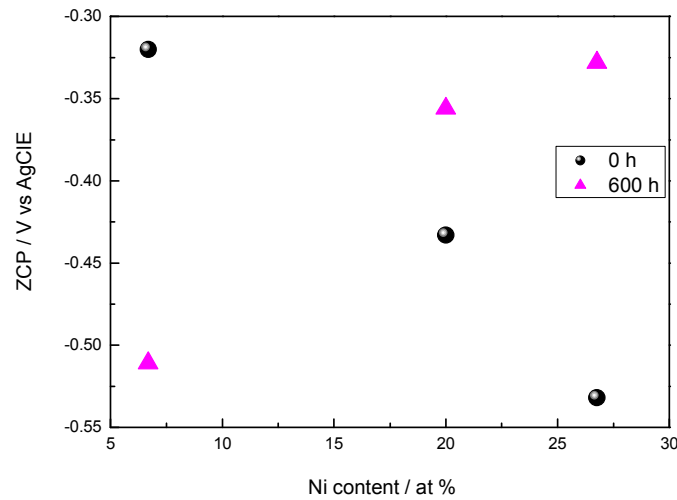
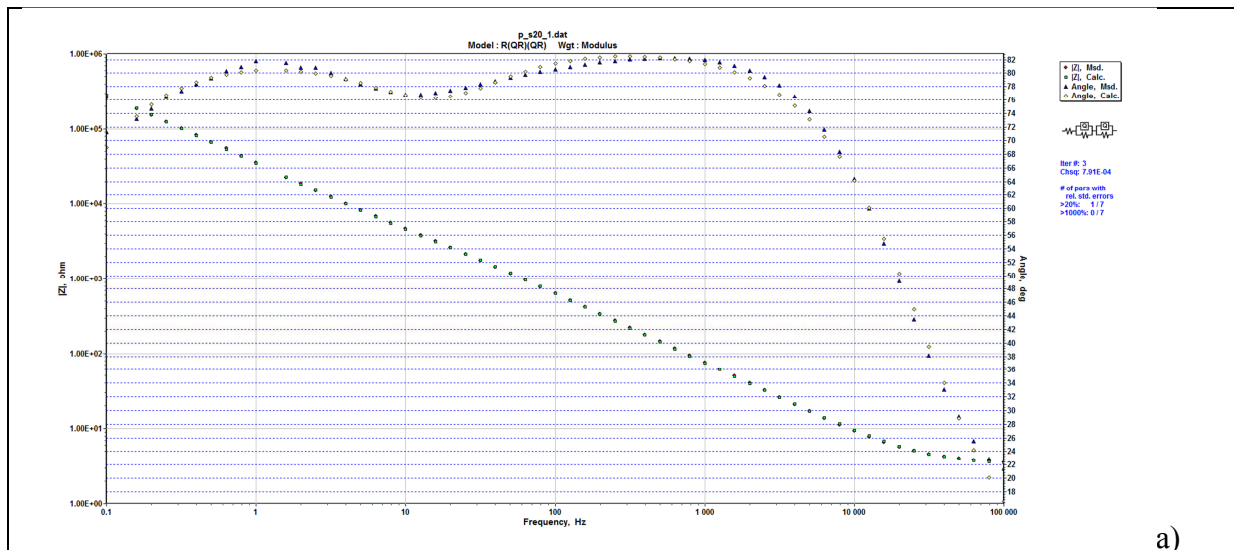


Fig 6 Dependence of ZCP vs Ni content for specimens anodized in sulphuric acid electrolyte and coloured by PRC in the different colouring electrolytes

Prepared selective layers can be characterised also by the EIS. Concerning *EIS measurements* two types of the specimens are interpreted. Aluminium substrate was anodized in sulphuric and phosphoric acid, respectively, following colouring with S marked electrolyte. Quantitative analysis of the experimental impedance data was performed by the non-linear least square method using ZsimWin 3.21 software. The constant phase element (Q) was used instead of an “ideal” capacitor to describe the response of the selective layers. Generally, the use of Q is due to the distribution of the relaxation times as a result of the inhomogeneity present on the microscopic level at the oxide/electrolyte interface and static disorders such as porosity.



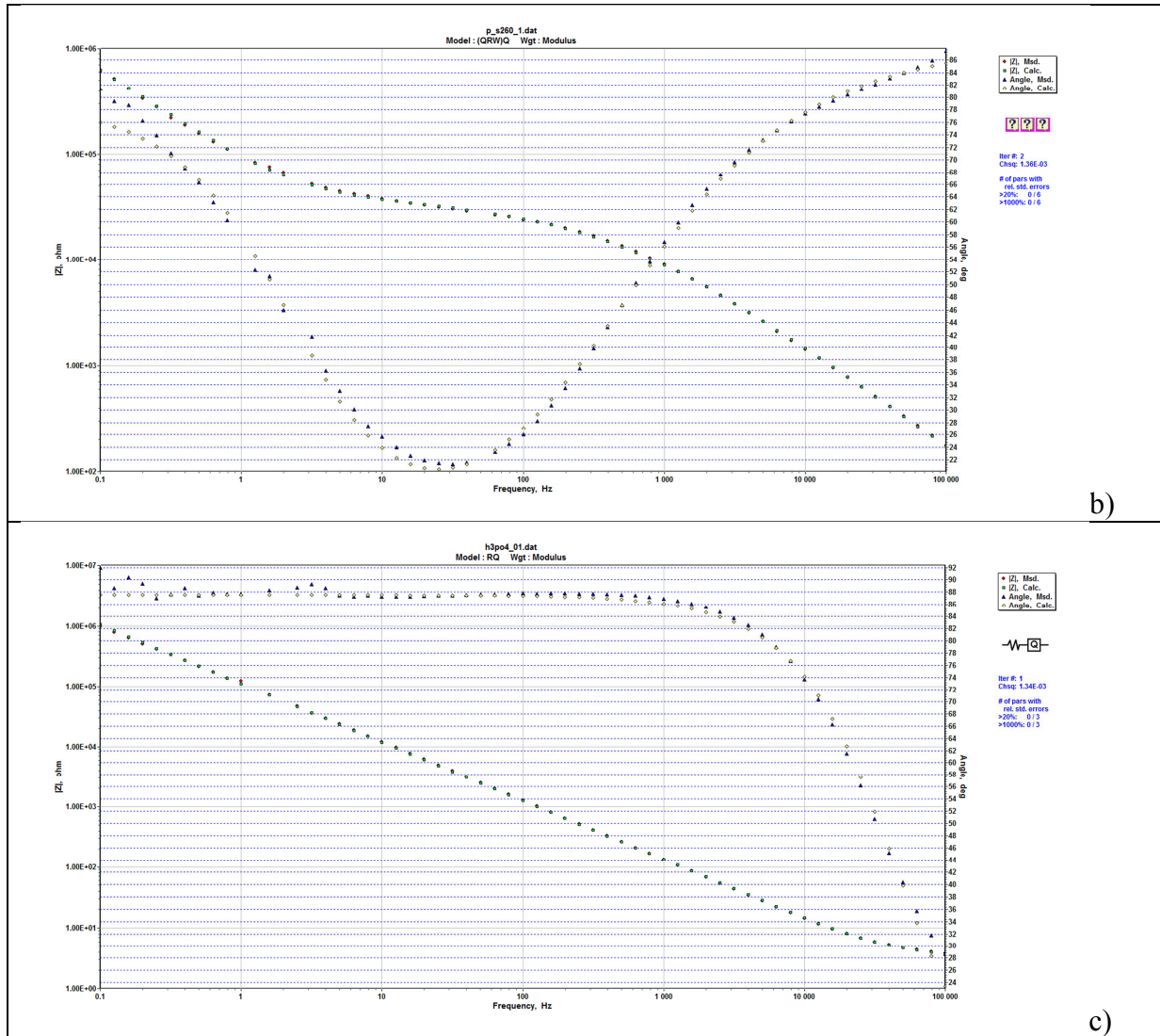


Fig 5 Bode plots of the finishes oxidized in a) sulphuric acid, b) sulphuric acid and exposed humidity, c) phosphoric acid electrolyte and coloured electrochemically in S marked electrolyte

In the case of sulphuric acid the impedance spectra may be described by a simple equivalent circuit model of type $R(QR)(QR)$ whose elements represent the different structural peculiarities of the porous and barrier layers (Fig. 7a). The calculated value for the equivalent circuit elements are characterised for thin narrow pores in upper layer and lower layer (barrier) with high electrical resistance ($M\Omega$). 600 hours hydration exposition completely changes the shape of the impedance spectrum (Fig. 7b) which is typical for sealed anodic film [8].

In the case of phosphoric acid the impedance spectra may be described by a simple equivalent circuit model of type $R(QR_s)$ which is typical for unsealed anodic film (Fig. 7c). The calculated value for the exponent n to Q is 0.973 ± 0.002 that is characteristic for relatively uniform surface with large pores [8].

All the obtained results are in a very good correlation indicating that primary role in the quality of the selective layer play the pore type formed after anodic oxidation. 20 μm high narrow pores in average of 20 nm are formed in sulphuric acid anodizing electrolyte. At the bottom of the pores nickel is deposited and upper pore walls are hydrated with humidity. The short 5 μm and wide pores in average of 30 nm are formed in phosphoric acid anodizing electrolyte. There is nickel electrodeposited on the surface in nods pattern and following reaction with humidity some intercalation products appeared forming $Ni(OH)_2$.

Acknowledgement

The financial support of the VEGA research project 1/0985/12 is greatly acknowledged.

References

- [1] Kennedy, C.E., 2002, *Review of Mid- to High-Temperature Solar Selective Absorber Materials*, NREL/TP- 520-31267, Golden, CO: National Renewable Energy Laboratory
- [2] Hansal, W.E.G., Sudipta, R., 2012, *Pulse Plating*, Bad Saulgau, National Eugen G. Leuze Verlag KG
- [3] Fairchild, M.D., 2005, *Color and Image Appearance Models*, Chichester UK, John Wiley and Sons
- [4] Nyquist, A.R., Kogel, O.R., 1971, *Infrared Spektra of Inorganic Compounds*, New York and London, Academia Press
- [5] Hermet, P., et al., *Physical Review B* 2011 (84) 23511-23517
- [6] Agrawal, A., et al., *Thin Solid Films* 1992 (221) 239-253
- [7] Chen, D., Giroud, F., Minter, S.D., *J. Electrochem. Soc.* 2014 161 (9) F933-F939, doi:10.1149/2.0811409 jes
- [8] Gonzáles, J.A., López, V., Bautista, A., Otero, E., Nóvoa, X.R., *J. Appl. Electrochem.* 1999 (29) 229-238

II. Corrosion of Nanoparticles

A lifetime of metallic nanoparticles in heat exchange liquids

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Keywords: nanofluids, metallic nanoparticles, corrosion, propylene glycol

Abstract. This work focuses on prediction of lifetime of metallic nanoparticles in heat exchange nanofluids. Copper, nickel and iron nanoparticles were studied in a 40 wt.% aqueous solution of potassium formate and propylene glycol. Materials were observed by means of mass loss exposure tests, linear polarization resistance and potentiodynamic measurements. Potassium formate solution is not a suitable bearing liquid for metallic nanoparticles. Propylene glycol seems promising, however additional corrosion prevention needs to be applied.

Introduction

The use of nanoparticles as an agent enhancing heat transfer of liquids is studied all over the world. Nanoparticles mostly increase the heat transfer coefficient of a liquid [1-7] and also slightly increase viscosity [1, 5, 8]. Some works focus on metallic nanoparticles [6, 7, 9-11]. The problem is that metallic nanoparticles have a lower thermodynamic stability of metallic nanoparticles [12, 13].

An estimation of the lifetime of metallic nanoparticles in heat exchange liquids used for solar collectors was the aim of this work.

Experimental

Sheets of pure nickel, copper and carbon steel (size 5 x 5 cm) were used as samples of a “macrosurface”. Fe nanoparticles were obtained as a commercial product (Nano Iron Ltd). Cu nanoparticles were prepared by gas atomization of AlCu40 alloy and subsequent dissolution of aluminium matrix in a 20 wt.% solution of sodium hydroxide. Nickel nanoparticles were prepared by melt spinning of AlNi20 alloy and subsequent dissolution in NaOH. The size of the nanoparticles was:

- Fe – 50 nm,
- Cu – 25 nm,
- Ni – 250 nm.

These bearing liquids were tested:

- 40 wt.% aqueous solution of potassium formate (HCOOK) and
- propylene glycol (PG).

Sheet samples were exposed to formate solution for 5 days and in propylene glycol for 189 days. A subsequent mass loss was estimated.

Electrochemical measurements were carried out on both types of samples (sheets and nanoparticles) after 16 hours of exposure to an environment. Sheets were measured in a pressure cell with an exposed area of 10 cm². Nanoparticles were immobilized on the surface of a paraffin-impregnated graphite electrode (PIGE). The nanoparticle surface was estimated by weighing the electrode before and after the immobilization, assuming half of each spherical nanoparticle was in contact with the environment. A saturated calomel electrode (SCE) was used as a reference and platinum wire as a counter electrode. Linear polarization resistance was measured in the range of -10 mV/E_{OC} to +10 mV/E_{OC} (E_{OC} = open circuit potential) with a polarization sweep rate of 0.1

mV.s^{-1} . Then the anodic potentiodynamic curve was measured in the range of $-50 \text{ mV}/E_{\text{OC}}$ to $+1000 \text{ mV}/\text{SCE}$ with a polarization sweep rate of 2 mV.s^{-1} . All measurements were carried out four times.

Results and Discussion

The corrosion rate of copper and nickel in 40 wt.% HCOOK solution was quite high (Fig. 1) and a lifetime would be practically unacceptable in the case of using such a bearing liquid. Propylene glycol shows better results. The corrosion rates are at least two orders lower (Fig. 2). Calculated lifetimes are given in Fig. 2 as well, and in the case of big nickel particles it approaches the economically acceptable lifetime of two years.

A comparison of electrochemical techniques in both bearing liquids is given in Figs. 3 and 4. Polarization resistances in HCOOK are approximately four orders lower when compared to propylene glycol (Fig. 3). Both materials are in an active state in HCOOK (Fig. 4). Nickel is suitable for passivation, but the corrosion rate would still be very high. Both materials are passive in propylene glycol (PG).

The results of the polarization resistance of macrosurfaces (sheets) and nanoparticles are compared in Fig. 5. Only copper provides comparable dissolution rates as nanoparticles, while nickel and iron are much more reactive when compared to the macrosurface.

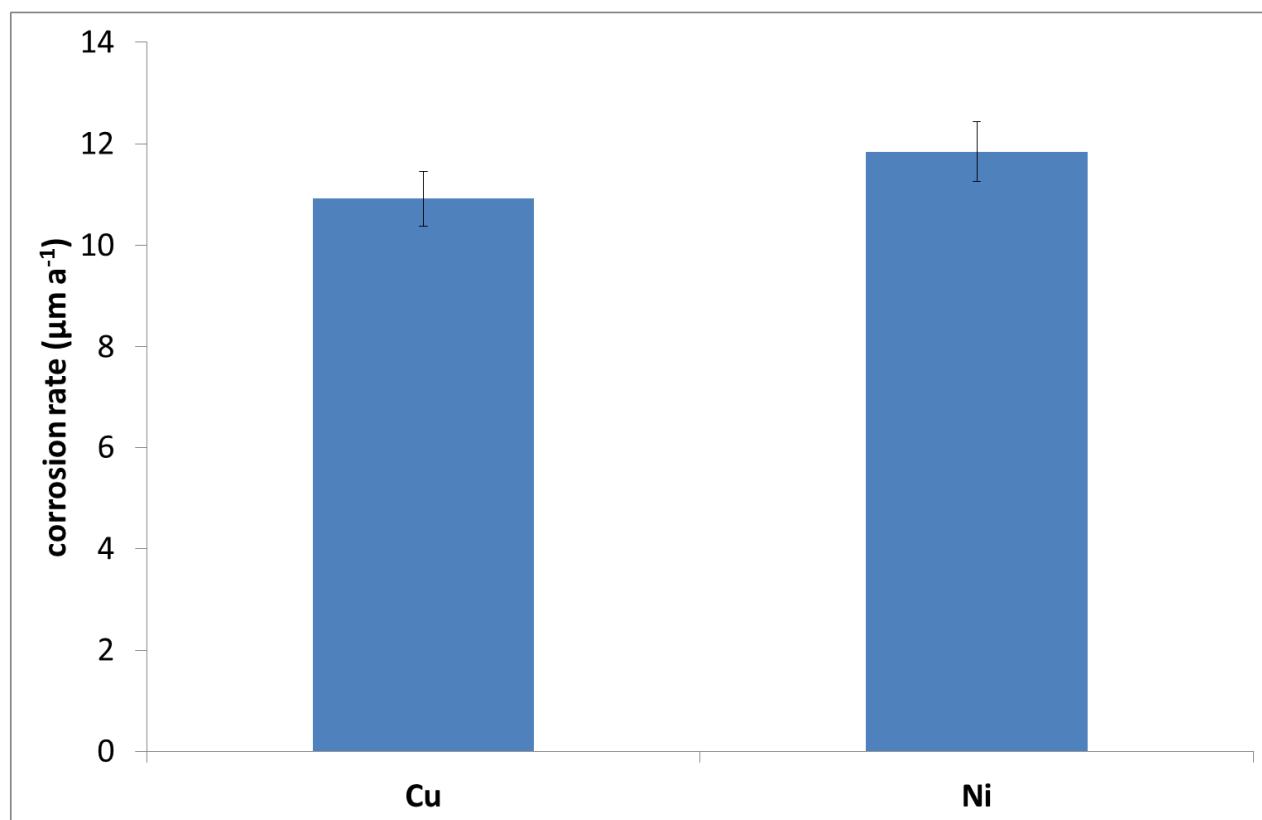


Fig. 1 Corrosion rate of sheets in 40 wt.% HCOOK estimated by mass loss.

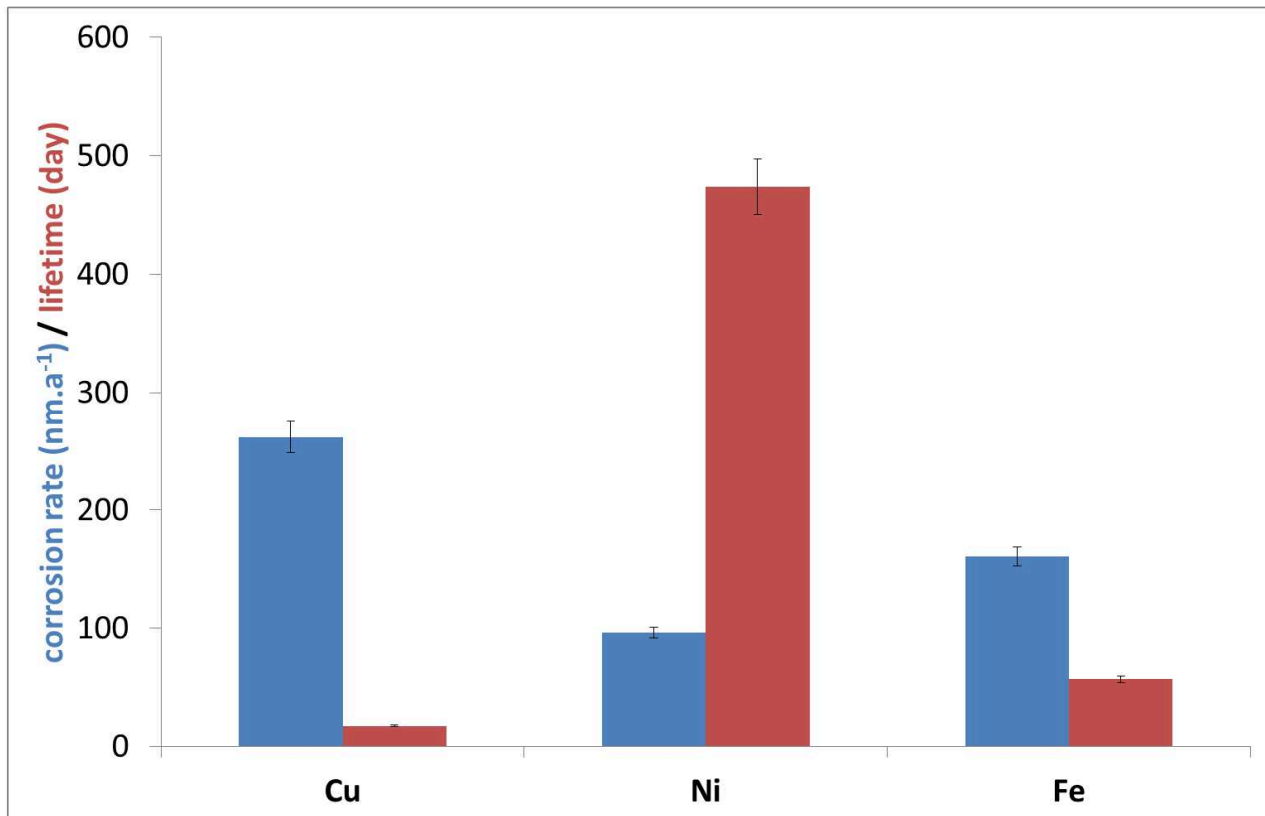


Fig. 2 Corrosion rate of sheets in propylene glycol estimated by mass loss and calculated lifetime of nanoparticles used in this work.

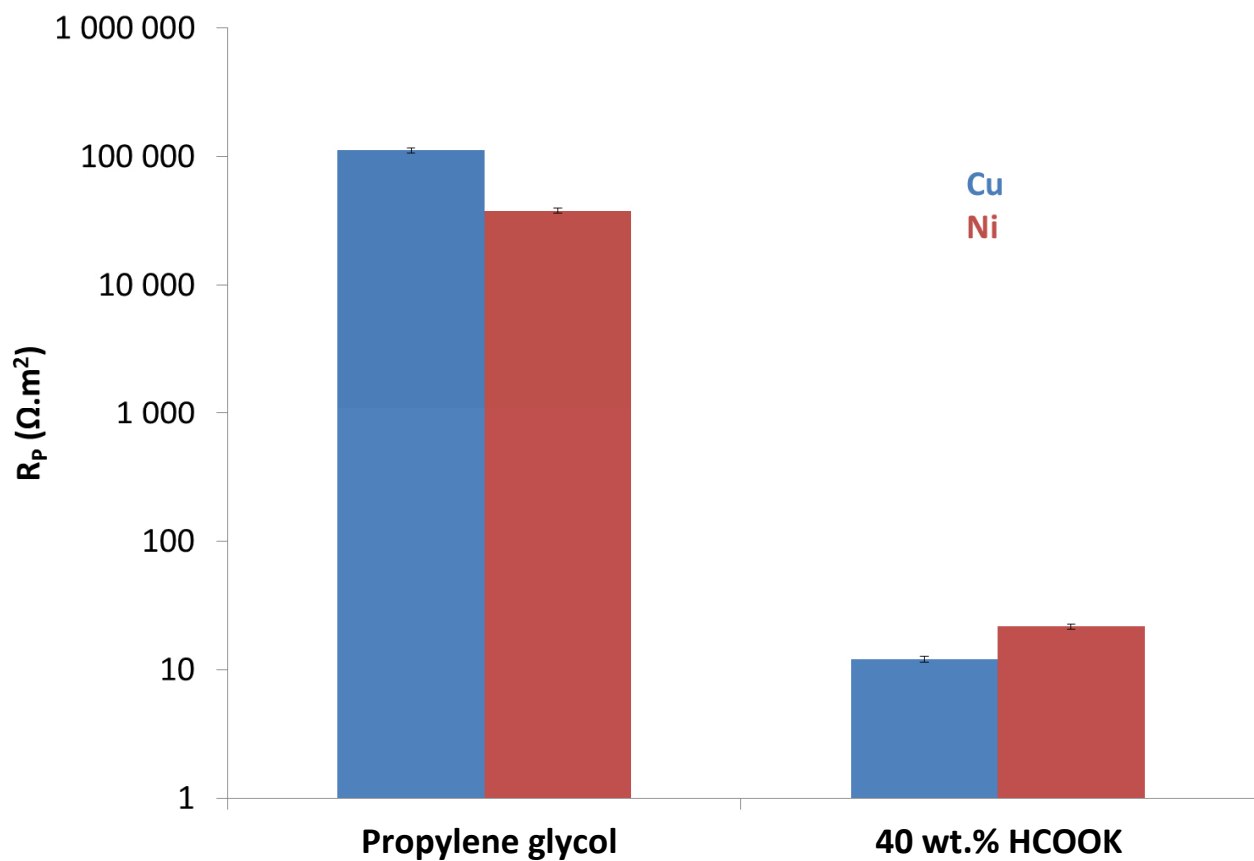


Fig. 3 Polarization resistance of nickel and copper in both bearing liquids.

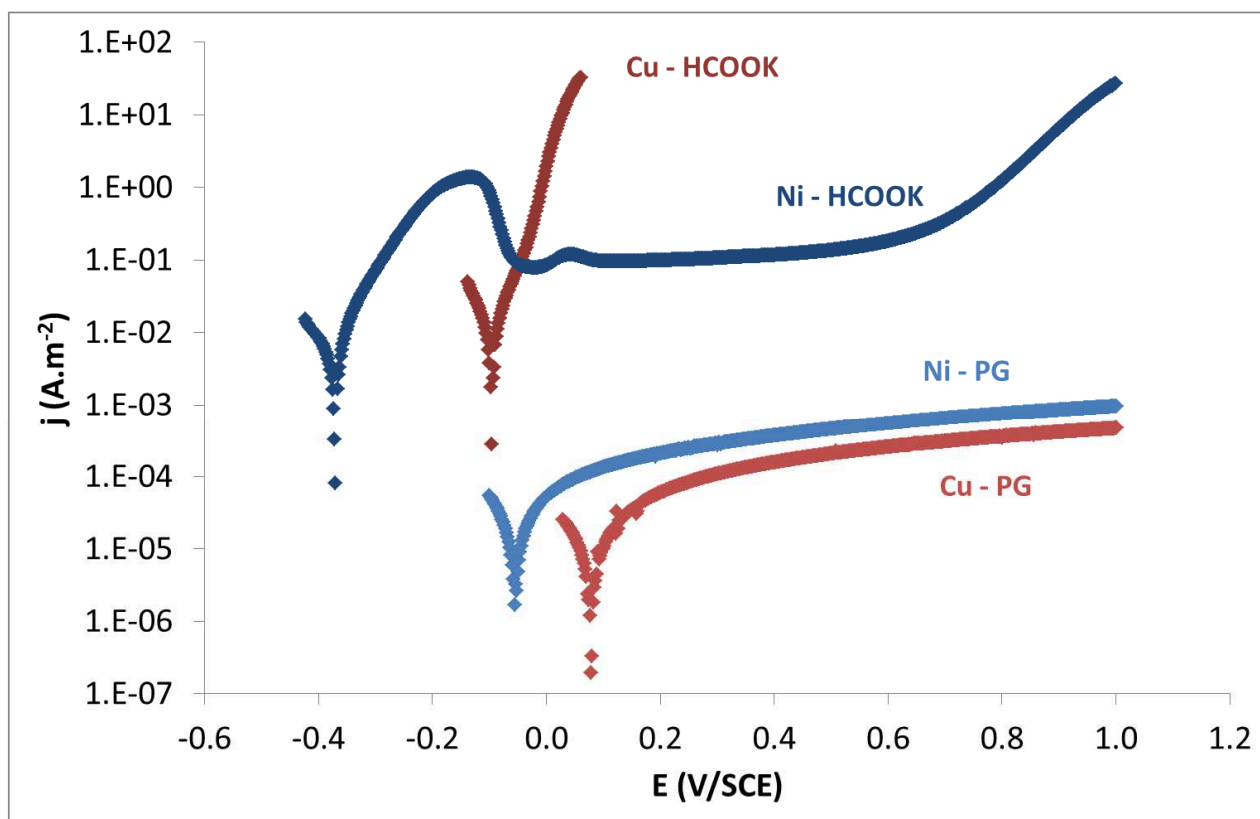


Fig. 4 Potentiodynamic curves of nickel and copper in both bearing liquids.

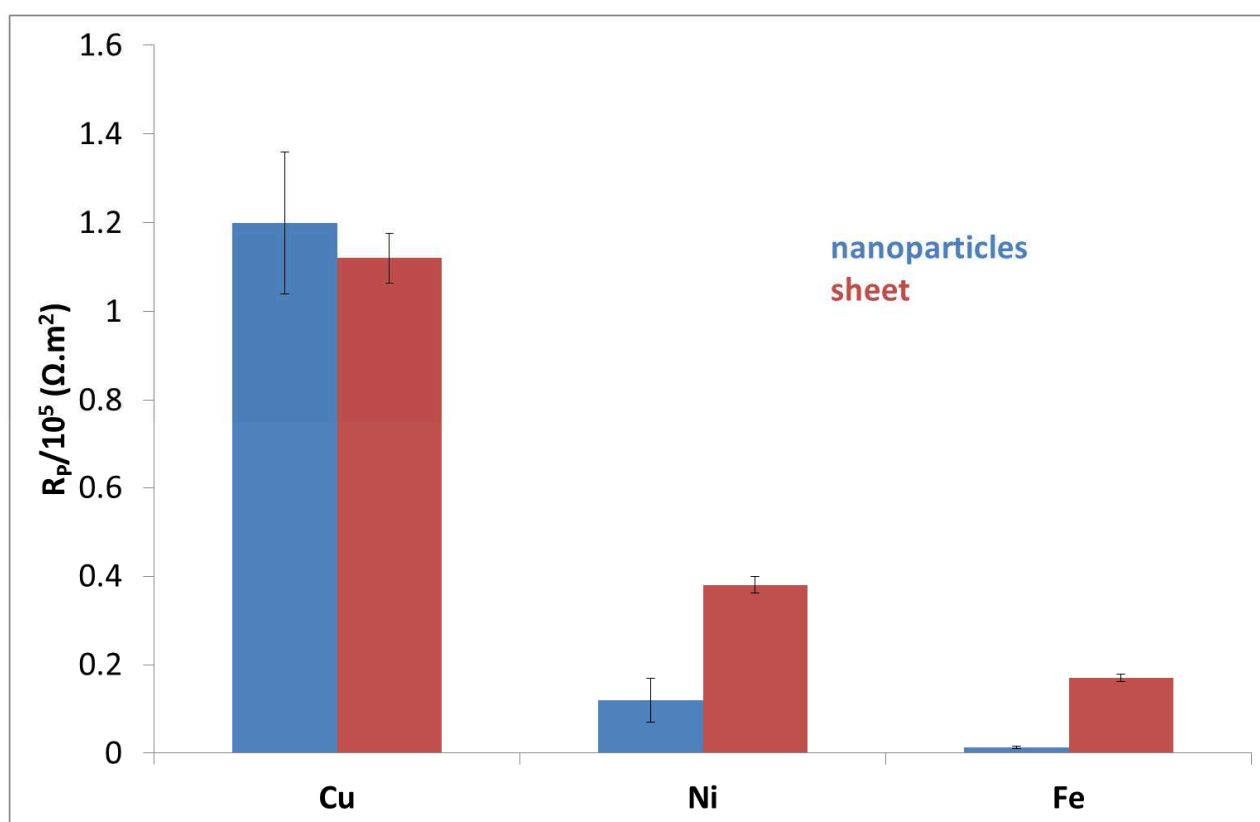


Fig. 5 Comparison of polarization resistance of sheets and nanoparticles in propylene glycol.

Conclusions

Aqueous solution of potassium formate is not a suitable bearing liquid for a heat exchange nanofluid due to its high aggressiveness.

Propylene glycol is a promising bearing liquid. The lifetime of nanoparticles is still not sufficient for practical use and it should be prolonged by some additional corrosion prevention such as inhibitors, surface treatment, etc.

Acknowledgement

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References

- [1] Z. Meng, D. Wu, L. Wang, H. Zhu, Q. Li, Carbon nanotube glycol nanofluids: Photo-thermal properties, thermal conductivities and rheological behavior, *Particuology*, 10 (2012) 614-618.
- [2] I. Palabiyik, Z. Musina, S. Witharana, Y. Ding, Dispersion stability and thermal conductivity of propylene glycol-based nanofluids, *Journal of Nanoparticle Research*, 13 (2011) 5049-5055.
- [3] R. Saidur, K.Y. Leong, H.A. Mohammad, A review on applications and challenges of nanofluids, *Renewable and Sustainable Energy Reviews*, 15 (2011) 1646-1668.
- [4] E.V. Timofeeva, W. Yu, D.M. France, D. Singh, J.L. Routbort, Base fluid and temperature effects on the heat transfer characteristics of SiC in ethylene glycol/H₂O and H₂O nanofluids, *Journal of Applied Physics*, 109 (2011) 014914.
- [5] H. Xie, W. Yu, W. Chen, MgO nanofluids: higher thermal conductivity and lower viscosity among ethylene glycol-based nanofluids containing oxide nanoparticles, *Journal of Experimental Nanoscience*, 5 (2010) 463-472.
- [6] Y. Xuan, Q. Li, Heat transfer enhancement of nanofluids, *International Journal of Heat and Fluid Flow* 21 (2000) 58-64.
- [7] J.-C. Yang, F.-C. Li, Y.-R. He, Y.-M. Huang, B.-C. Jiang, Experimental study on the characteristics of heat transfer and flow resistance in turbulent pipe flows of viscoelastic-fluid-based Cu nanofluid, *International Journal of Heat and Mass Transfer*, 62 (2013) 303-313.
- [8] G. Żyła, M. Cholewa, A. Witek, Rheological properties of diethylene glycol-based MgAl₂O₄ nanofluids, *RSC Advances*, 3 (2013) 6429.
- [9] R. Kathiravan, R. Kumar, A. Gupta, R. Chandra, Preparation and pool boiling characteristics of copper nanofluids over a flat plate heater, *International Journal of Heat and Mass Transfer*, 53 (2010) 1673-1681.
- [10] V. Suryanaryanan, R.T. Tom, A.S. Nair, T. Pradeep, Electrochemical investigations of oxide coated nanoparticles, *Proceedings of the National Academy of Sciences A*, 70 (2004) 483-488.
- [11] X. Wei, L. Wang, Synthesis and thermal conductivity of microfluidic copper nanofluids, *Particuology*, 8 (2010) 262-271.
- [12] J. Leitner, M. Kamarádek, Termodynamický popis nanosystémů, *Chemické Listy*, 107 (2013) 606-613.
- [13] L. Tang, X. Li, R.C. Cammarata, C. Friesen, K. Sieradzki, Electrochemical Stability of Elemental Metal Nanoparticles, *Journal of American Chemical Society*, 132 (2010) 11722-11726.

III. Failure Analysis

Corrosion Protection Of Infrastructure Of Power Industry

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Keywords: atmospheric corrosion, corrosion protection, service life prediction, long-term exposure

Abstract SVUOM specialists have participated in many activities concerning corrosion failure analysis or testing the materials/coatings for corrosion protection in power industry (e.g. temporary protection of various parts of power plants, long-term corrosion behaviour of weathering steels and mild steel with hot dip galvanised coating (HDG) and paint coatings of poles, reconstruction of parts of nuclear plants, etc.). There are many materials and corrosion protective coatings used for infrastructure of power industry – the SVUOM main interest is focused to distribution network.

Introduction

Nearly all materials exposed to atmosphere are susceptible to changes of their physical integrity (often using the terms physic-chemical transformations, corrosion, weathering) due to effects from their environment. The extent of the corrosion processes can be predicted, when the affecting parameters and the mechanisms of the processes are known. In reality this prediction capacity is very limited, because the full process of atmospheric corrosion is not understood in all details. With experimentally derived dose-response functions it is possible, however, to obtain a rough risk assessment for some materials.

Background corrosion rate of metallic materials (carbon steel, weathering steel, zinc coating, aluminium) exposed at atmospheric environment may be predicted according to EN ISO 9223 and EN ISO 9224. Prediction models based on dose response (D/R) functions express the effects of environmental and climatic parameters on the corrosion of a material. These D/R functions had been used for mapping of corrosion loss of structural metals in the Czech Republic (CZ).

The studies performed in SVUOM showed that the actual corrosion rate of structural metals quickly reacts on decreasing of SO₂ [1]. The surfaces exposed in high polluted environment slowed the corrosion rate in case of SO₂ pollution had been reduced in atmosphere. This significant change of SO₂ in atmospheric environment of CZ occurred during short period 1990-95 when the SO₂ decreased from ca 40 – 90 µg.m⁻³ to 10 – 20 µg.m⁻³. The most significant changed occurred at industrial localities.

Steel structures used in power industry infrastructure are exposed in atmospheric environment often with specific corrosion conditions that may significantly affect durability of corrosion protection (e.g. concentration of air pollutants, limited maintenance of structures, and chloride deposition in the road microclimate) [2]. Many structures and coatings showed long-term protective ability. On the other hand significant reduction of coatings lifetime still occurs due to several factors:

- improper structural design,
- defects in coatings,
- specific corrosion stress.

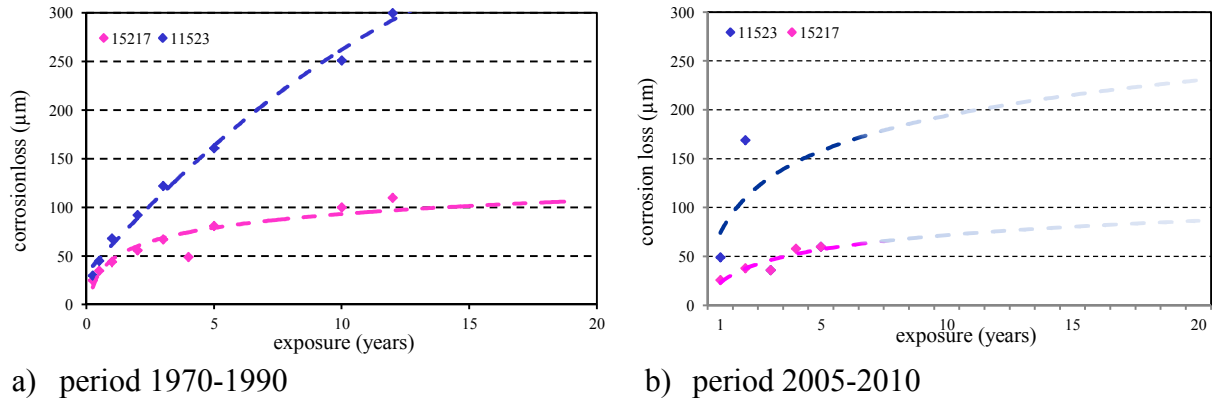
There is ca 160 000 km of the distribution network at the CZ. Corrosion protection of poles is performed by three systems:

- structural material is weathering steel (in 1970's there were built ca 4 000 poles and 130 switching stations),
- structural material is galvanised steel,
- structural material is carbon steel with painting systems.

In this paper the selected results of evaluation of power industry infrastructures from corrosion failure and durability point of view are presented. The field data are compared to prediction models.

1 Weathering steel structure durability

The application of weathering steel for the poles and other infrastructure of power industry is the most extended use of this material in the CZ. Due to decreasing of air pollution the average corrosion rate of the weathering steel decreased too (Fig. 1).



a) period 1970-1990 b) period 2005-2010
 Fig. 1 Corrosion loss of carbon (11523) and weathering (15217) steels in industrial atmospheres in different SO_2 pollution level in the CZ

In case the recommended design and other addition protective means had been applied during poles construction (painting the structures till ca 1 m from ground (Fig. 2a), painting the inner surfaces of laps (Fig. 2c, etc.), the durability of these structures increased as the protective patina layers with thickness ca 120 μm and suitable chemical composition had been formed on them [3, 4].

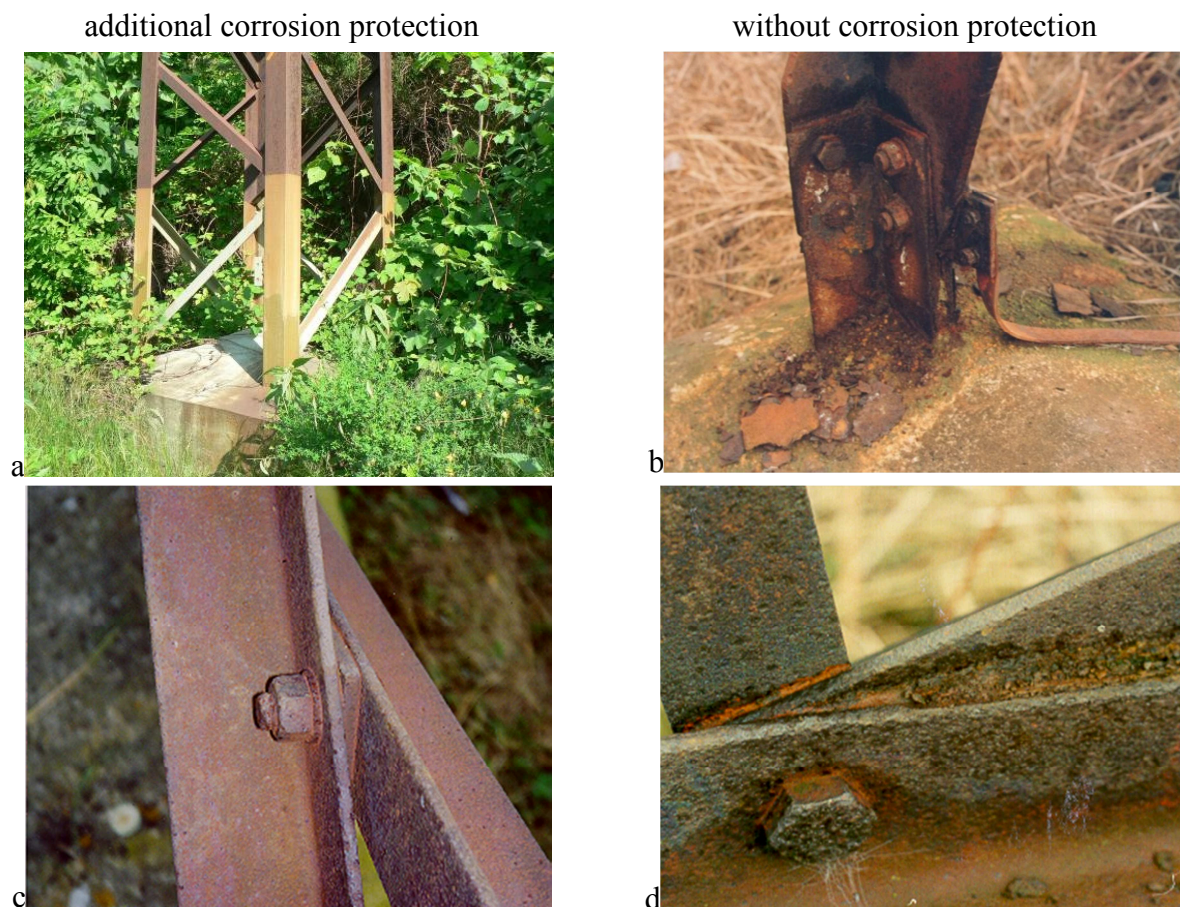


Fig. 2 Corrosion behaviour of weathering steel structures

The corrosion problems occurred in case of non-suitable design of poles (Figs. 2b and 2d). The additional corrosion protective means as special sealing and painting systems had been applied to these details but their efficiency and durability strongly depend on quality of surface treatment and carefulness of applications work – in the case of the most proper cleaned surface the durability of corrosion protection is 15 years [5]. With other surface treatment the corrosion of steel occurred after ca 5 years of exposure (Fig. 3). The painting of total area of these structures is not suitable due to problems with continuity of the paint coatings (Fig. 4). When some discontinuities (mechanical damages, pores, cracks) are in the coating, the wetness is accumulated in these damaged points and the weathering steel corrodes. Some problems may also occur due to difficulty with surface treatment before application. Under the paint layer the active corrosion occurs when the patina layer had been mechanically removed before paint application and water diffusing through paint layer creates conditions non suitable for patina forming.

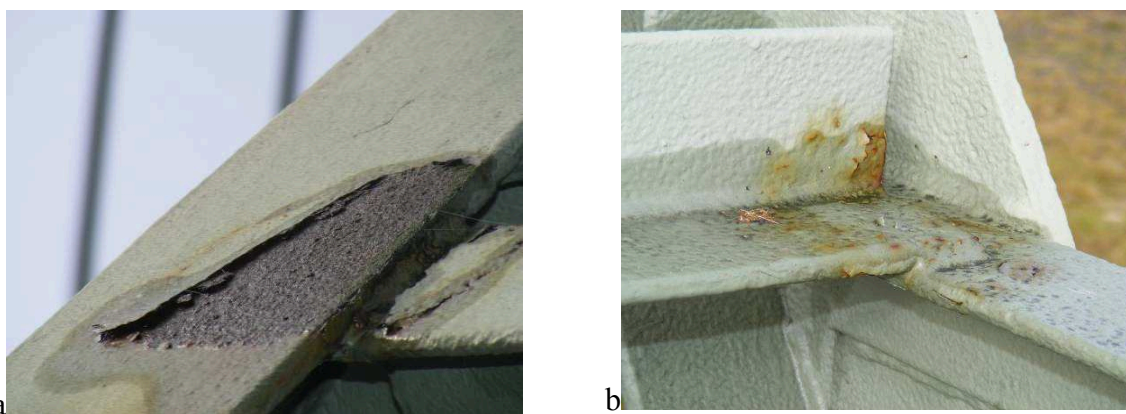


Fig. 3 Failure of paint systems applied on weathering steel structures after 5 years of exposure

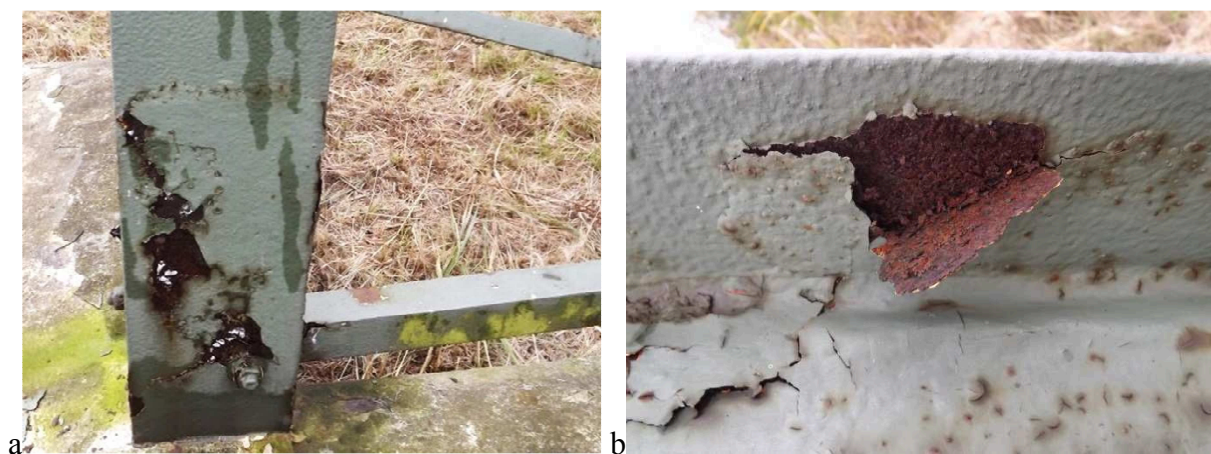


Fig. 4 Paint system on weathering steel (total surface painting) after 11 years of exposure

The durability of properly designed poles from weathering steel is higher than planned (30 years) and it should be increased by application of additional protective means in case of localised corrosion attack. In the CZ many weathering steel poles are exposed more than 40 years, without additional paints, and they are in good condition.

2 Galvanised steel structure durability

The galvanization of iron and steel products is chosen as corrosion protection of power industry infrastructure for its low cost, low maintenance demands, long life, sustainability and aesthetics. Rate of corrosion attack of construction materials including zinc coatings can be estimated from data of atmospheric corrosivity (EN ISO 9223, EN ISO 9224, EN ISO 14713) [6]. The actual

average yearly zinc corrosion mass loss in the CZ is $1.2 \mu\text{m}$ maximally. The corrosivity is in category C2 for rural and urban environments and in category C3 for industrial environments (Fig. 5 – locality of field study is indicated). Currently zinc and zinc coatings lifetime is relatively high depending on their thickness in normal atmospheric environment in the CZ.

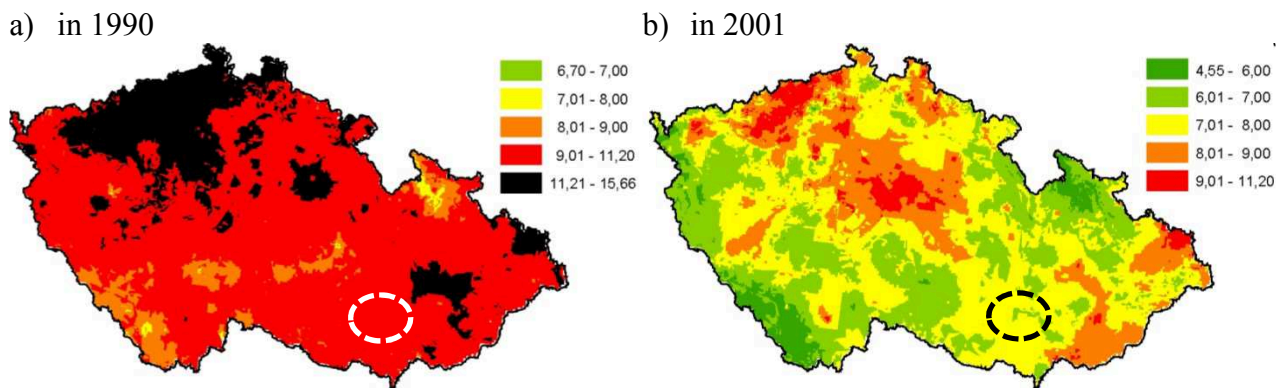


Fig. 5 Yearly corrosion loss of zinc (g.m^{-2})

The HDG coatings on poles were controlled after 10, 20, 30 and 40 years in localities around Brno city (Fig. 6). The residual thickness of zinc coating was measured on selected profiles of these truss structures. As the lower phases of HDG coating with certain amount of iron (min. 10% Fe) were exposed to atmosphere the surface of structure shows the rusted appearance. After 40 years of exposure the residual zinc coating thickness were ca $100 \mu\text{m}$ on diagonals. For estimation of corrosion behaviour of HDG coating on these structures the original thickness values are very important information – these values differ according to thickness of profile wall, galvanisers, etc.. The reference structures were poles after ca 4 years of exposure which surface show still the gloss zinc coating with zinc blossom and no corrosion layers. This assumption may be a source of uncertainty of corrosion behaviour model (Fig. 7).

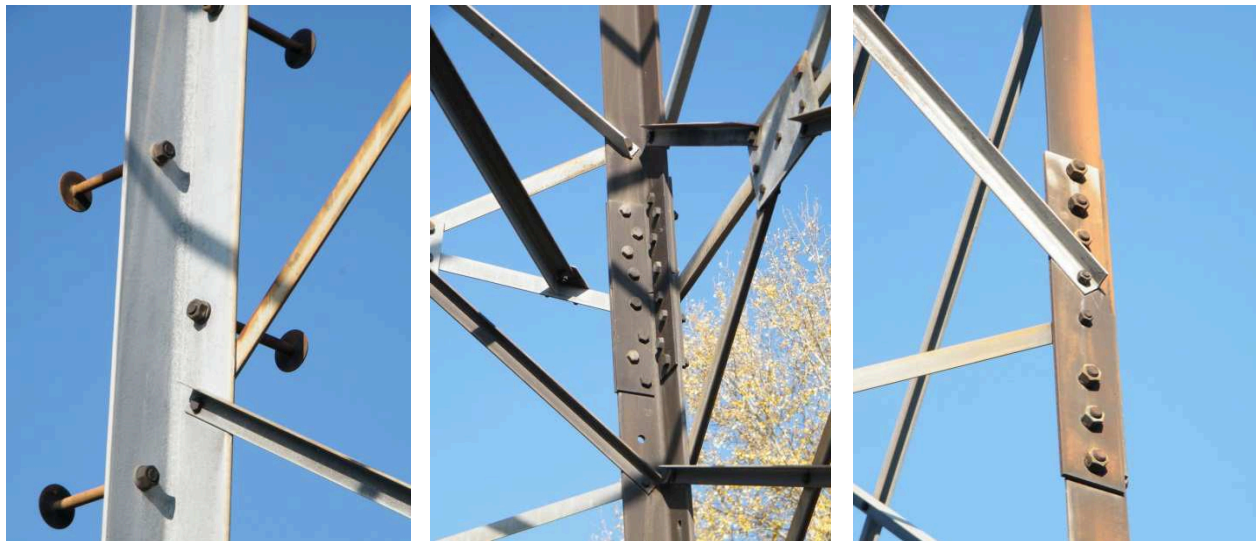


Fig. 6 Examples of HDG coating surface on poles

According to this field study the corrosion rate of HDG coating is ca $1.4 \mu\text{m.a}^{-1}$. This is in good fitting to long-term corrosion rate according to EN ISO 9224 (Table 1) if the model of initiate higher corrosion rate due to high SO_2 is used. From measured values the decreasing of zinc coating corrosion since 1990 (ca 15 years of exposure) may be illustrated. In industrial localities of the CZ the decreasing of HDG corrosion rate would be significant. Other explanation for this higher durability of HDG coating is higher corrosion resistance of intermetallic iron alloyed lower layers of HDG coatings [7]. The accurate values for atmospheric environments are not estimated. The

expected service life to first maintenance is still ca 20 years to obtained residual HDG thickness 25 – 30 μm for additional application of paint systems as duplex corrosion protection according to EN ISO 1461 (Table 1).

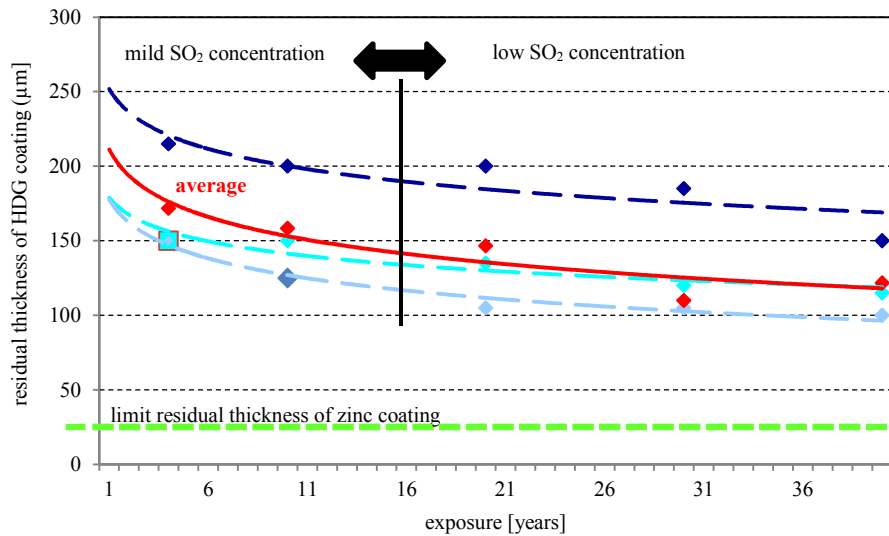


Fig. 7 Decreasing of residual HDG coating on different elements of truss structure of poles

Table 1 Corrosion loss of zinc according to EN ISO 9223 and EN ISO 9224

corrosivity category	yearly corrosion loss r_{corr} [μm]	steady corrosion loss [μm]			
		10 years	20 years	30 years	40 years
C3 	0.7 ~ 2.1	13.6	24.0	37.6	48.0
C4	2.1 ~ 4.2	27.3	48.0	75.3	96.0

The zinc corrosion failure due to mechanism of bimetallic corrosion had been found on gusset plates (joining armatures) of poles as the copper alloy cotter pins had been used (Fig. 8).

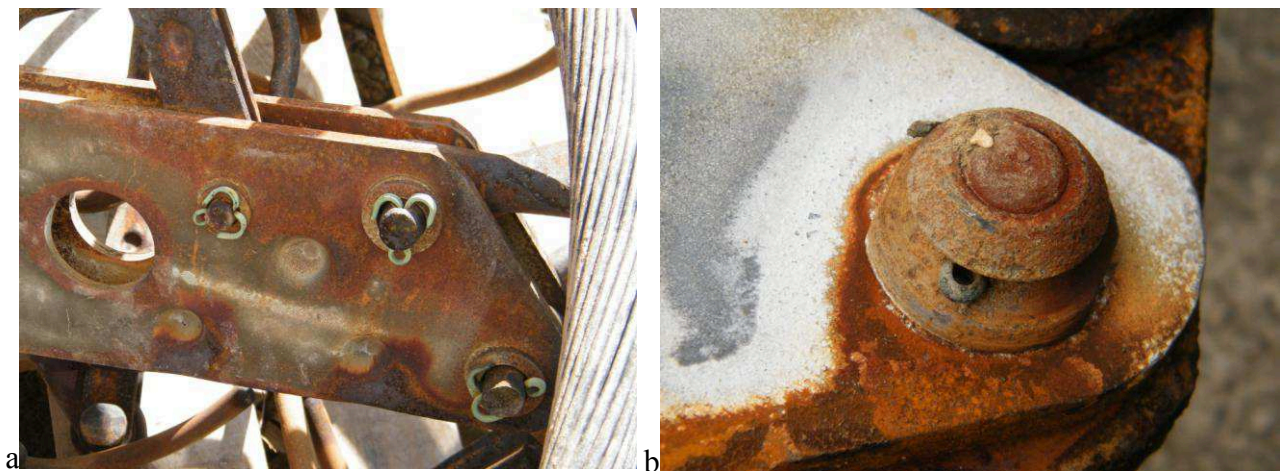


Fig. 8 Intensive corrosion of zinc coating in contact with copper ions

Significant parts of power distribution network are conductors and overhead earth wires. Generally three conductors are required per AC 3-phase circuit, although single-phase and DC circuits are also carried on poles. Overhead electrical power transmission conductors, constructed

from aluminium wires centrally reinforced by galvanized steel strands, have been evaluated after 40 and 50 years of exposure and specific types of corrosion form was identified. For each material/coating the long-term corrosion prediction model was proposed [6, 7]. Standard EN 50189 relates to round galvanized steel wires used for construction of conductors of outdoor transmission lines. This standard specifies requirements for mass of zinc coating on wires (Table 2).

Table 2 Mass and thickness of zinc coating for wire with given diameter

diameter d [mm]	class				
	A	B	C	D	E
	mass of coating [g.m^{-2}]				
$2,00 \leq d < 2,25$	215	430	175	550	215
$2,25 \leq d < 2,75$	230	460	190	640	250
$2,75 \leq d < 3,20$	230	460	190	640	250

Phase conductors VVN consist from few layers of aluminium wires and cross lay strand from galvanised steel wires. There were evaluated two types of phase conductor with various exposures:

- type 450AlFe8 exposed for ca 40 years in industrial atmosphere with high corrosivity in period 1973-1995 - the white corrosion products occurred on all wires of cross lay strands and corrosion of substrate steel occurred on 50% of evaluated areas with various intensities,
- type 450AlFe6 exposed for ca 50 years in rural atmosphere with low corrosivity - the white corrosion products occurred on all wires of cross lay strands and corrosion of substrate steel occurred on 30% of evaluated areas with various intensities.

The overhead earth wires from VVN lines are type 70FeZn consisting from 1+6+12 galvanised steel wires with diameter 2.10 mm. Evaluated wires were exposed for 20 years (since 1992) in locality with corrosivity degree C3/C2. The very thin grey layer of zinc corrosion products covered the majority of galvanised steel wires surface. Sporadically there were found small spots of substrate steel corrosion products on external surface of few wires, probably on areas of mechanical damage of wires. There were also evident voluminous white layers of zinc corrosion products (Fig. 9a). The surface of internal galvanised wires was covered by voluminous layer of white corrosion product and dust deposits (Fig. 9b).

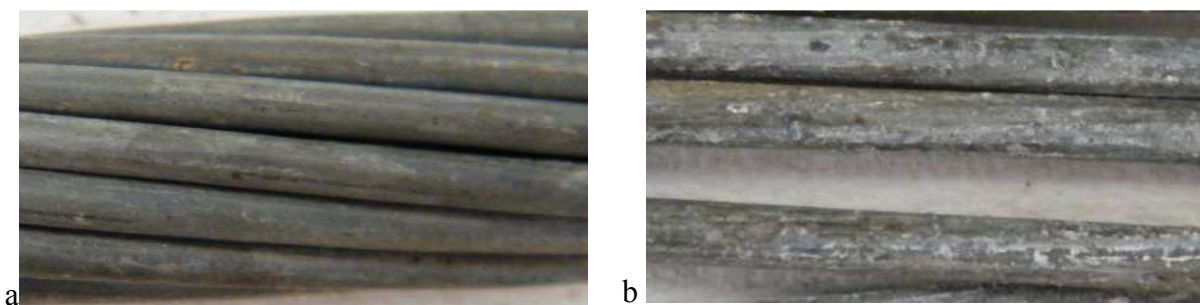


Fig. 9 Appearance of galvanised overhead earth wires ((a) outer and (b) inner stands)

There were not found phase η in residual layers of zinc coating which thickness varied from 50 μm to locally totally corroded coating. The corrosion rate of zinc coating of all type of conductors and earth wires was estimated by the statistical treatment of measured values of residual thickness of zinc coating:

- wires of inner strands – $2.5 - 4.0 \mu\text{m.a}^{-1}$,
- wires of outer strands – $3.5 - 7.5 \mu\text{m.a}^{-1}$.

Estimated corrosion rate of zinc coatings on wires is ca 3 to 5 times higher than corrosion rate of zinc according to standard EN ISO 9224. Increasing of corrosion rate of zinc coating is due to the

structure of rope, respectively rope winding/construction, which allows longer impact of wetness than on flat surfaces. The lower number of wires in ropes is better for corrosion resistance.

3 Aluminium overhead conductors' durability

As mentioned above the conductors consist from 2 or 3 layers of aluminium wires. The evaluated conductors are described above, too.

The surfaces of aluminium wires of outer strands are covered by layer of aluminium corrosion products; the inner strands' surfaces are covered mainly with dust deposits. Dominant compounds are duct particles SiO_2 and aluminium oxide Al_2O_3 . As significant element of surface layers the sulphur had been identified.

Uniform corrosion of aluminium ca 20 μm after 40 years exposure in industrial atmospheres is not the decisive mechanism of aluminium wires durability degradation. On investigated conductors the localised forms of corrosion had been found – pitting and intercrystalline corrosion (Table 3 and Fig. 10).

Prediction of localised form of aluminium corrosion is difficult – there is only limited number of long-term studies of these forms of corrosion in specific atmospheric environments. The average values of pitting corrosion 50 μm correspond to published data of aluminium coupons exposed in industrial atmospheres [10]. The depth of pitting corrosion decreased with time of exposure. For intercrystalline corrosion there is no data available. The mechanical stress was supposed to be a dominant reason of premature breaking of conductor.

Table 3 Depth of localised corrosion attack

layer of stand	corrosion form	maximum depth [μm]	
		50 years/450AlFe6	40 years/450AlFe8
A (outer)	pitting	200	200
	intercrystalline	150	n
B (inner)	pitting	300	150
	intercrystalline	60	200
C (inner)	pitting	-	50
	intercrystalline	-	n

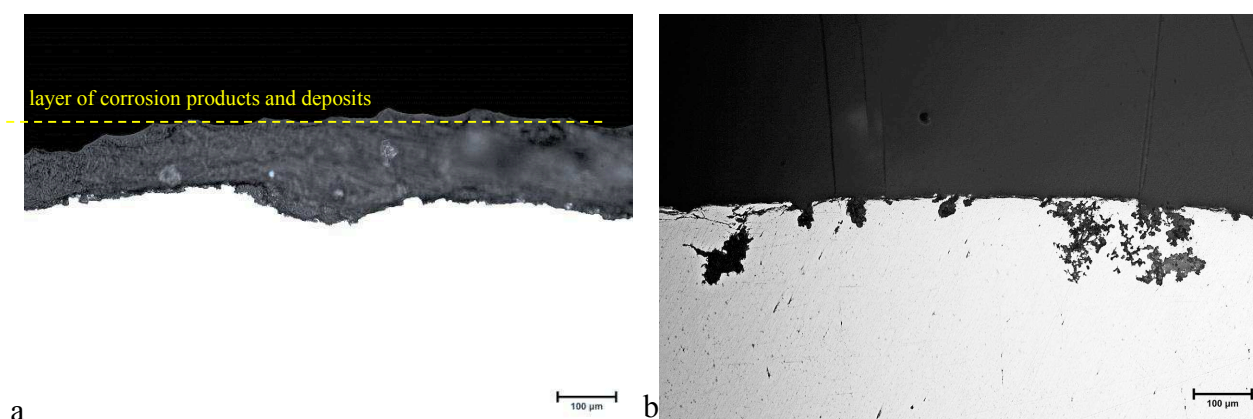


Fig. 10 Various forms of aluminium (a) uniform and (b) localised corrosion

4 Painting systems' durability

For poles and other structures many different types of paints are applied during last ca 40 years. The corrosion protection was made by any types of coatings system. First it was paint system with minium primer (Pb_3O_4). Next applied system was 2-component epoxy coating. Contemporary one

component coatings based on acrylic or modified alkyd resin are commonly used. Complicatedness of the construction is eliminated using tree layers systems.

There is any prediction model for degradation of painting systems such as developed for metallic materials – their service life is estimated on the results of accelerated laboratory corrosion tests according to ISO 12944-6. Durability of paint systems is defined in 3 categories: low (L) 2 to 5 years, medium (M) 5 to 15 years and high (H) more than 15 years. The condition of the paint system applied can be assessed by use of ISO 4628-1, ISO 4628-2, ISO 4628-3, ISO 4628-4, ISO 4628-5 and ISO 4628-6. It has been assumed that the first major maintenance of painting would normally need to be carried out for reasons of corrosion protection once the coating has reached Ri 3 (rusting of 1% of structural surface) as defined in ISO 4628-3.

Coating of paint systems are degraded mainly by chalking, cracking, peeling and rusting mechanism. Blistering had been found on painted poles and other infrastructure exceptionally. Some examples of paint failure are given in Fig. 11. In many cases the recommendation of Ri 3 degree of rusting was not kept.



Fig. 11 Examples of failure of painting systems

Due to changes of paint systems applied during ca 40 years the test of compatibility is necessary to perform before repainting. In case of low compatibility between the “old” and “new” paints, the new applied system maybe shows visual problem very quickly – immediately or after 24 hrs after application (Fig. 12).

Conclusion

Without the power industry, no other industrial sector could exist, that makes the power industry the largest in the world in terms of the number and value of projects and facilities. As aging infrastructure in the CZ and as the durability of this infrastructure planned as long-term as possible, the field investigation of long-term exposed structures is very important for decision making procedure for this strategic sector.

The prediction models according to EN ISO 9223/9224 and other derived standards may be used for prediction of durability of metallic materials/coatings for power industry infrastructures exposed in atmospheric environments. There is necessary to verify these models in respect to structure

designs, specific microclimates, corrosion mechanisms and other factors influencing the corrosion stress.

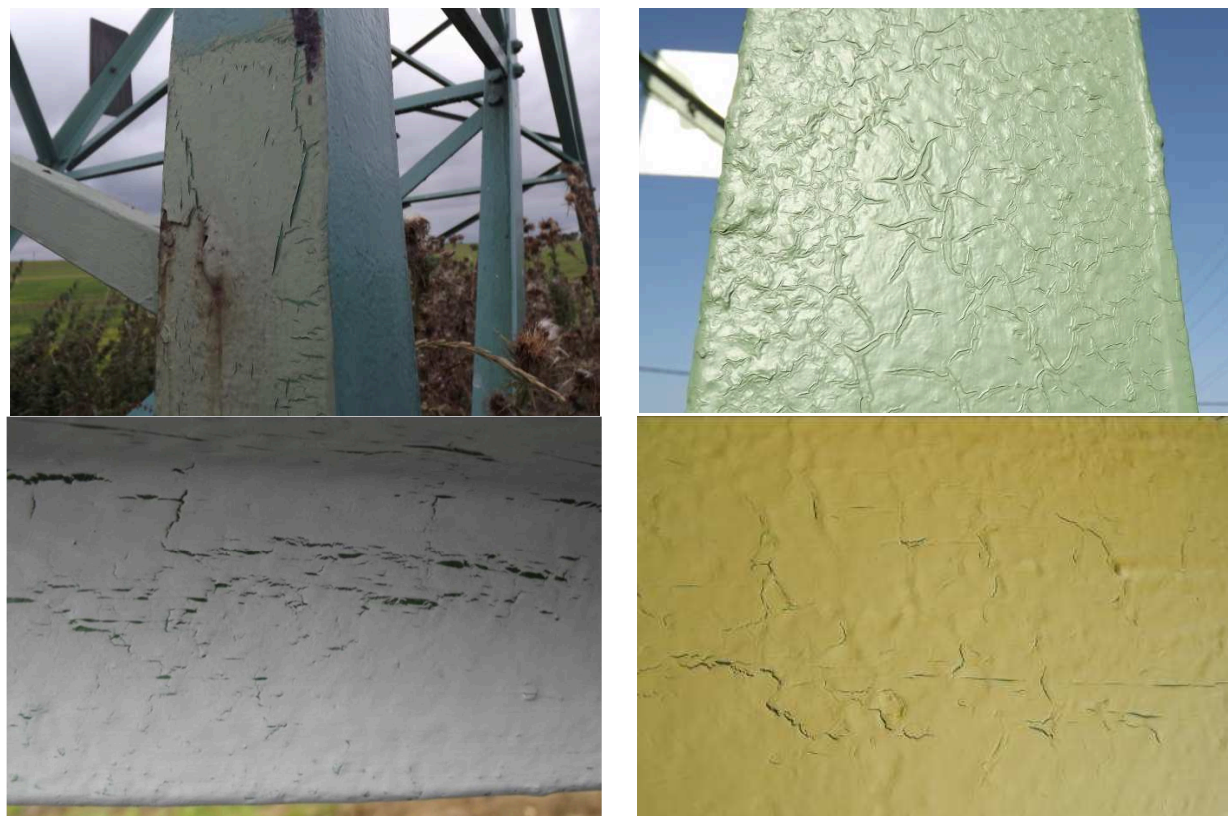


Fig. 12 Examples of non-compatible paint systems

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References

- [1] K. Kreislova, D. Knotkova, L. Kopecky: Changes in corrosion rates in atmospheres with changing corrosivity, in *Corrosion Engineering, Science and Technology*, Vol. 44, No. 6, 2009, ISSN 1478-422X, pp. 433-440
- [2] K. Kreislova, Contemporary condition of corrosion attack of metallurgical products and its evaluation, proceedings of METAL2013 – 22nd international conference of metallurgy and materials, 15 - 17 May 2013, Brno, Czech Republic
- [3] K. Kreislova, D. Knotkova, A. Koukalova, V. Krivy, L. Rozlivka, J. Podjuklova, T. Lanik, Corrosion behaviour of weathering steels in the Czech republic, proceedings of 2nd International conference Corrosion and Material Protection, ISBN 978-80-903933-6-3, 19-22 April 2010, Prague
- [4] K.Kreislova, D.Knotkova, T.Kubatik, J.Had, P.Sajdl, Properties and protective ability of long-term exposed weathering steel constructions in the Czech Republic, proceeding of EUROCORR 2010, 13-17.9.2010, Moskva
- [5] D.Knotkova, J.Vlckova, Atmospheric Corrosion of Bolted Lap Joints Made of Weathering Steels, *Atmospheric Corrosion*, ASTM 1239, W. W. Kirk and Herbert H. Lawson, Eds., American Society for Testing and Materials, West Conshohocken, PA, USA, 1995, pp. 114 – 136
- [6] K.Kreislova, Zinc coatings lifetime determination in the atmospheric environment, proceedings of INTERGALVA conference, Paris, June 11 – 14.2012

- [7] A.P. Yadav, H. Katayama, K. Noda, H. Masuda, A. Nishikata, T. Tsuru, Effect of Fe–Zn alloy layer on the corrosion resistance of galvanized steel in chloride containing environments, *Corrosion Science* 01/2007; 49(9), pp. 3716-3731
- [8] V. Sklenicka, K. Kreislova, J. Brejcha, Evaluation of overhead line components, 2013 INMR World Congress, 8. - 11. September 2013, Vancouver, Canada
- [9] K.Kreislova, J. Kvapil, M. Jaglova, L. Turek, M. Paraková, Hot dip galvanised coatings on wires and ropes, proceeding of 19th conference of galvanising, 2.-4.10.2013, Spindleruv Mlyn, Czech Republic, ISBN 978-80-905298-1-6, pp. 104- 119
- [10] C.Vargel, *Corrosion of Aluminium*, Elsevier:Oxford, 2004

CORROSION DEGRADATION OF STEEL PIPES IN INDIRECT COOLING CIRCUIT OF GAS CLEANING

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Abstract:

The paper deals with corrosion damage of steel pipes which were a part of the indirect cooling circuit of gas cleaning. The pipes were made of steel ASTM A106 Gr.B. The outer surface of pipes of the inside part of the circuit was affected by flue gases with mean temperature of approximately 1200 °C. The pipes of the outside part of the circuit were exposed to outer environment with mean temperature of about 25 °C. The cooling water flowing in these pipes had mean temperature of about 20 °C and contained a corrosion inhibitor based on zinc chloride (with addition of hydrochloric acid, phosphoric acid and 2-phosphonobutane -1,2,4 – tricarboxylic (PBTC)). Flow rate of cooling water was 3700 m³/h, its total volume 1500 m³, and the pressure of cooling water was 600 kPa. The achieved thickening of cooling water was N=4. Side filtering was accomplished by a filter DPF 4000. The pipes of the cooling circuit were welded to each other, which initiated stress stimulating development of cracks on the outer surface of pipes in the heat-affected zone, Fig.1. The existing technological conditions resulted in formation of deposits on the outer pipe surfaces. Their presence changed thermal conditions in steel pipes.

Introduction

Failures of cooling circuits which are part of power industry equipment are frequently associated with loss of integrity of pipes and subsequent development of cracks at thermally most exposed sites. [1-3]. Initiation of cracks is related to a directed penetration of oxidation at planes of maximum tensile stress. The cracks parallel with the longitudinal axis of pipes are affected by excess tension due to internal overpressure; transverse cracks develop most frequently as a result of fatigue stress acting on the material undergoing thermal dilatation [4-6]. In both cases, the cracks act as concentrators of stress and potential sites of final failure of pipe walls.

Analysed material

The analysis of corrosion damage was carried out on steel pipes from the indirect cooling circuit of gas cleaning. The pipes were made from steel ASTM A106 Gr.B (0.25 % C, 0.27-0.93 % Mn, 0.1 % Si). The outer diameter of pipes was 89.9 mm and wall thickness 7.6 mm. The indirect cooling circuit was put in operation in October 2011, and visible cracks on the surface of pipes were observed in June 2013. The surface of pipes of the outside part of the circuit was affected by the outer environment to which the pipes were exposed, i.e. atmosphere with mean temperature of approximately 25 °C. The temperature gradient between the outer environment and the cooling water flowing inside these pipes was max. 8 °C. The outer surface of pipes of the inside part of the circuit was affected by flue gases with mean temperature of about 1200°C. The cooling water flowing in these pipes had mean temperature of 20 °C and contained a corrosion inhibitor KURITA S-6200, which, has been supplied by Kurita Europe GmbH since 2010 [7]. The flow rate of cooling water was 3700 m³/h and the total volume of flowing water amounted was to 1500 m³. Pressure of the flowing water reached 600 kPa. The thickening factor of cooling water was N = 4 (the

recommended thickening factor is $N = 4.5$). Side filtering was accomplished by a twin-chamber filter DPF 4000.

Methods of analysis of corrosion degradation of pipes

The methods of analysis of steel pipe specimens included standard procedures commonly used for evaluation of corrosion attack on metal materials. The initial examination was based on macroscopic analysis of the character and extent of corrosive damage to pipes. In the second stage, we used microscopic analysis in order to reveal the structure of the analysed material and character of its corrosion degradation. The analysis was carried out using a light microscope OLYMPUS VANOX-T. In order to determine chemical composition of corrosion products deposited on surface of steel, we used energy dispersive X-ray analysis (EDX) employing an analyser INCA in association with a scanning electron microscope JEOL JSM 7000F.

Results and discussion

Fig. 1 shows a part of the cooling circuit, namely the outer surface of pipes affected by flue gases. This figure shows an uneven layer of massive deposits produced by reaction of the metal surface with flue gases. Additional analysis was carried out on material sampled from the pipe at the site shown in Fig. 1.



Fig. 1 Outer surface of pipe affected by flue gases.

Macroscopic analysis

Fig. 2 shows the outer surface of *pipe 2*, which was affected by the environment in the facility where the circuit was installed. It was a covered production hall with mean annual temperature of approximately 25 °C. Fig. 3 shows the surface of *pipe 2* with deposited corrosion products at the site of damage marked with an arrow in Fig. 2.

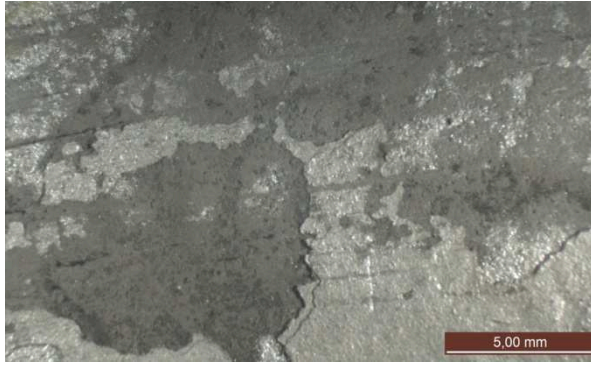


Fig. 2 Outer surface of *pipe 2* (exposed to environment in production hall)



Fig. 3 Detailed picture of the outer surface of *pipe 2* at the site marked with an arrow in Fig. 2.



Fig. 4 Corrosion layer deposited on inner surface of *pipe 2*



Fig. 5 Detail of the corrosion layer with a network of minute cracks at the site marked with an arrow

The inner surface of *pipe 2* is depicted in Figs. 4 and 5. Corrosion products formed a relief, uneven, and relatively heterogeneous layer. In several places, one could be observed a network of minute cracks in the corrosion layer (at the site marked with an arrow in Fig. 5).

Figures 6 and 7 show the surface of *pipe 3*, which was affected during operation by flowing flue gases of temperature approximately 1200 °C. The surface of this pipe was covered with thick, relief, corrosion layer, furrowed with parallel cracks running mostly transversally to pipe axis. The cracks developed due to the existence of thermal stresses resulting from thermal fatigue of the material in the corrosive flue gases environment. The way of joining the pipes (welding) within the assembly (Fig. 1), contributed to the stress by adding a tensile component associated with this corrosion-mechanical stressing.



Fig. 6 Outer *pipe* surface (exposed to flue gases)



Fig. 7 Detail of corrosion layer (shown in Fig. 6) with minute cracks on pipe surface

Corrosion damage to the inner surface of *pipe* 3, Figs. 8 and 9 was shown by production of a corrosion layer with rough surface and presence of tubercles (marked with an arrow in Fig. 9). The development of tubercles, as a demonstration of oxygen corrosion, is associated with the action of oxygen and concurrent effect of aggressive salts added to cooling water in the system.



Fig. 8 Inner surface of *pipe* 3



Fig. 9 Detailed picture of the inner surface of *pipe* 3 with tubercles

Microscopic analysis

Microscopic analysis was carried out on cross-section specimens prepared from the examined pipes. Fig.10 shows the outer surface of *pipe* 2, covered with a thin, approximately 100 μm layer of corrosion products at the site of damage to the metal coat (see Fig. 3). The inner surface of *pipe* 2 is depicted in Fig. 11. The corrosion layer is uneven. Corrosion penetrated into the steel to a maximum depth of about 100 μm . With regard to the thickness of the pipe wall (7.6 mm) the damage presented no significant corrosion risk.

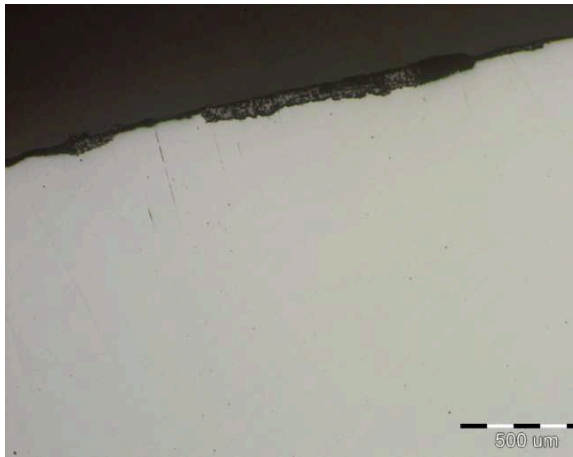


Fig. 10 Corrosion layer deposited on the outer surface of *pipe 2*

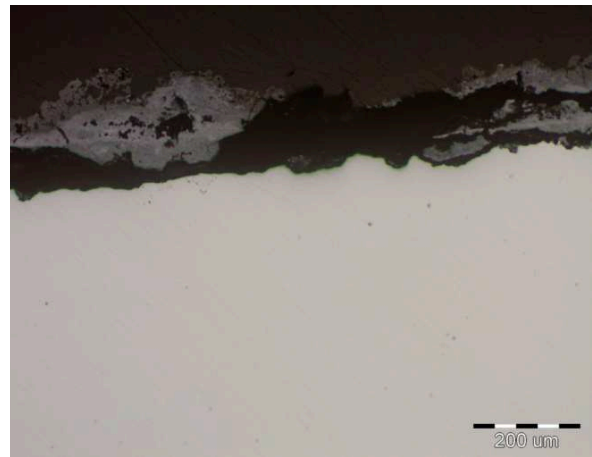


Fig. 11 Corrosion layer on the inner surface of *pipe 2*, penetrating into steel to a maximum depth of 100 μm

With regard to the extent of corrosion damage, only *pipe 3* was analysed in an etched state. After etching, one could observe the course of cracks (Figs. 12 and 13) running from the surface into the steel structure. The maximum depth of cracks (in the examined specimen) approached approximately 2.3 mm, which constituted more than 30 % of the pipe wall thickness. The cracks followed a straight line (no branching was observed) which corresponded to corrosion damage – stress-directed oxidation – at relatively high levels of the tensile component of stress. The inner surface of *pipe 3* exhibited corrosion damage characteristic of combined action of oxygen and the chlorides and sulphates present in the circulating cooling water.

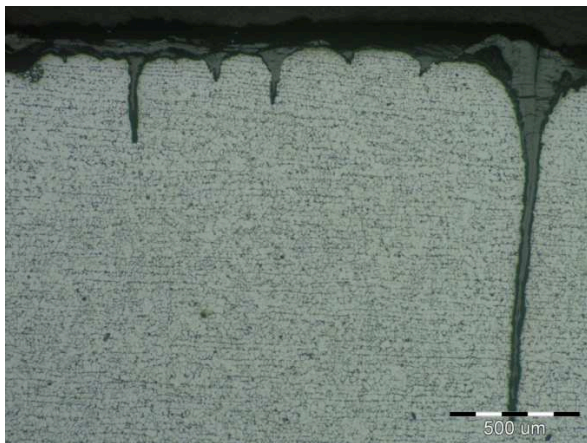


Fig. 12 Outer surface of *pipe 3* with cracks penetreating into the steel

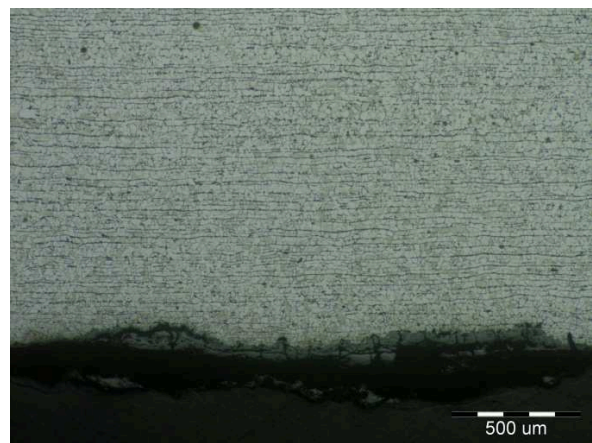


Fig. 13 Inner surface of *pipe 3* with deposited corrosion layer

Energy-dispersion (EDX) analysis of corrosion damage of pipe 3

Because *pipe 3* was most damaged by corrosion, the corrosion layer inside the crack of this pipe and on its surface was subjected to EDX analysis (Figs. 14 and 15). Analysed were also samples of corrosion products deposited on the outer surface of pipes which was affected by flue gases. Summary of results of analyses – including those not documented in this paper – is presented in Tab. 1.

Table 1 EDX analysis of corrosion layer deposited on the outer surface of pipe 3

	Inside the crack		On crack surface	
	Spectrum 4	Spectrum 5	Spectrum 7	Spectrum 8
Element	wt. %			
O	25.1	2.6	25.5	28.2
Si	0.4	0.2	0.3	0.5
S	2.7	0.9	0.5	0.2
Cl	2.4	1.1	2.2	23.2
K	0.2	-	-	-
Ca	0.7	0.2	-	-
Fe	46.3	58.6	65.3	45.6
Zn	22.3	14.4	6.3	0.7

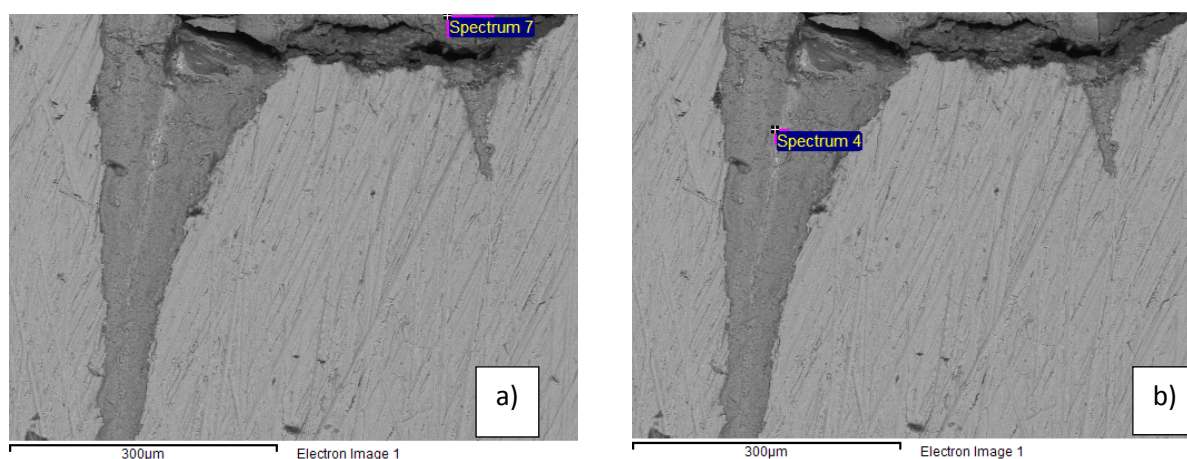


Fig. 14: EDX analysis of corrosion layer: a) inside the crack, b) on crack surface

The chemical composition presented in Table 1 shows that iron and oxygen were the dominant elements in corrosion products. They formed iron oxides which were produced in the process of high-temperature corrosion on the outer surface of *pipe 3*. Results of EDX analysis of the inner surface of *pipe 3*, presented in Table 2, show that corrosion layer on this surface consists mostly of Fe and O, which are part of produced oxides. They developed by reaction between cooling water and the inner surface of steel pipe. In addition to components such as Mn, Al, Si, and partially P and S, which are present in steel and water (part of the inhibitor), the corrosion layer, also contained components such as Mg, Ca, and P that were part of the cooling water.

Tab. 2 EDX analysis of corrosion layer on inner surface of *pipe 3*

Element in wt. %	Spectrum 82	Spectrum 83
O	28.8	29.9
Mg	0.4	0.7
Al	0.3	0.3
Si	1.1	1.2
S	0.3	0.3
Cl	-	0.3
Ca	2.8	2.7
Fe	51.4	47.7
P	2.6	2.9
Mn	0.3	0.4
Zn	12.1	13.7

Conclusion

Analyses were carried out on steel pipes from the cooling circuit designed for indirect cooling of a gas cleaning system. The character and magnitude of the attack on individual parts of steel pipes depended on their localisation in the circuit.

The macroscopic, microscopic and EDX analysis of examined specimens allowed us to draw the following conclusions:

- the outer surface of the analysed *specimen 2*, which was affected only by atmosphere in the production hall (not by flue gases) where the circuit was installed, was covered with corrosion layer which was produced by reaction between the environment and the steel surface: however, the extent and character of damage did not indicate important corrosion risk,
- the outer surface of *specimen 3*, which was exposed to flowing flue gases, was covered by massive layer of corrosion products, with crack zones oriented perpendicularly to the pipe axis,
- due to their composition, the flue gases were aggressive, which was manifested by chemical composition of deposited corrosion layer, produced by reaction between steel surface and flue gases. The biggest risk resulted from the presence of Cl, S, and alkaline metals, namely Na and K, and from Ca and heavy metals, such as Zn and Pb. The presence of these components supported development of volatile metal chlorides and low-melting eutectics in the deposited layer, which resulted in formation of deep furrows on steel surface,
- Fe and O were the dominant components of corrosion products. They were present in the form of iron oxides, which produced a heterogeneous layer unable to protect surface of steel against further oxidation by flue gases,
- in addition to surface corrosion, stress developed in the most strained parts of the circuit. Their origin was related to the way of joining the pipes in the circuit assembly (predisposition to the tensile component of stress), non-uniform temperature field on the outer side (non-uniform flow of flue gases) and temperature gradient with regard to the side that was in contact with cooling water flowing in the pipes.
In comparison with the outer surface, the character of damage to the inner surface of pipes differed due to the action of cooling water on steel surface.
- the inner surface of pipes was covered with a corrosion layer with localised tubercles (best visible on inner surface of *specimen 3*) which developed under the action of oxygen present in cooling water, in combination with other aggressive components, such as chlorides and sulphates,

The following causes of corrosion attack on inner surface of cooling circuit pipes could be considered:

- failure to comply with the recommended chemical regimen of treatment of circulating cooling water,
- low flow rate of cooling water,
- higher temperature of the inner surface of pipe wall exposed to flue gases.

Generally, these factors affect negatively the low-carbon, non-alloyed steel despite its anti-corrosion protection based on the use of corrosion inhibitor.

References

- [1] S. Tuleja, J. Kocich, Corrosion-erosion damage of an evaporater, Corrosion in Power Industry. 2006, 30. – 31.5.2014, Košice, Slovakia, 86-89
- [2] G. Baki, et al, Thermal History and Stress State of a Fresh Steam-Pipeline Influencing its remaining service life, Thermal Science. 15 (2011) 3, 691-704
- [3] M. Djukic, et al, Probability of Failure of Thermal Power Plant Boiler Tubing System Due to Corrosion, FME Transactions. 35 (2007) 47-54
- [4] A. Bhatia, Science and Reactor Fundamentals – Materials. CNSC Technical Training Group
- [5] N. J. Al-Mudeer, et al, Basrah Journal of Science (C). 24 (2006) 35 - 47
- [6] B. R. Cardoso, et al, Microstructural Degradation of Boiler Tubes Due to the Presence of Internal Oxide Layer, J. Mater. Res. Technol. 1 (2012)
- [7] J. Lukáč, J. Vanovčan, The analysis of extreme corrosion degradation causes of heat exchanger, Corrosion in Power Industry. 2006, 30. – 31.5.2006, Košice, Slovakia, 62-67

Atmosphere Aggressivity State Mapping in Slovak Republic for Corrosion of Construction Materials

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Keywords: map of corrosion, multi-pollution of atmosphere, concrete, corrosion, materials, copper, carbon steel, zinc.

Abstract. The paper is focused on the effect of multi-pollution of atmosphere on the construction materials degradation in the Slovak Republic. Corrosion increases the risk of failure, which has considerable impact on maintenance costs. The objective of the article is a creation of the proposal that should be used for processing of the corrosion maps for the various construction materials. It uses dose-response function that was developed based on long-term research. The corrosion map does not help to protect materials; however it can be useful for prediction of risks by design and analysis. The research done by the other researchers is taken into account also in our work. The results would be used as a basis for the beginning of a long-term research work.

Introduction

Degradation of not only metallic materials, but also other construction materials (concrete, glass, etc.) by chemical or physicochemical environmental treatment is an increasingly serious problem not only in Slovakia, but all over the world. The atmosphere and ultimately the hydrosphere could be particularly polluted by industrial activity, thus causing an increased corrosion aggressivity of atmosphere [1,2].

Almost all materials used for constructions or in engineering industry are subjected to corrosion. The result of this physicochemical reaction is a permanent change of the material that changes chemical, physical and mechanical properties. The actual exhibition of corrosion attack is usually very diverse and depends on the nature of metal, glass, polymers, composites, environment and all external and internal factors, which have an impact on the material [1,3,4].

Damage to structural materials caused by corrosion process will involve considerable costs for refurbishment. For example, the corrosion of structural steel is a major problem facing civil engineers engaged in the maintenance of aging infrastructure. Potentially corrosion rehabilitation is a very large market for those who would develop the expertise to deal with the problem [5].

For most materials, the corrosion mass loss is obvious, but if it causes significant structural damage, such as cracks, spalling, corrosion discoloration or other signs of deterioration in reinforcement concrete, or degradation of the concrete itself, it may raise the questions to what extent the damage is serious, what causes it and how to remedy the situation. There are many possible causes of distress; they include movement of the foundations, structural overloading, accidental damage, sulphate attack and alkali aggregate reaction, as well as the active corrosion [6].

Many countries show huge financial resources used for the reconstruction of interstate expressways, especially the bridges that are in winter subjected to a strong influence of chloride ions. Administrators of bridges situated near the sea shore have similar or even much bigger problems. Report on the costs of deicing (Transportation Research Board, 1991), the annual cost of bridge deck repairs was estimated to be \$50 to \$200 million, with substructures and other components requiring \$100 million a year and a further \$50 to \$150 million a year spent on multistory car parks. In the United Kingdom, these costs are estimated at more than £ 600 million a year. The statistics for Europe, the Asian Pacific countries and Australia are similar [5].

Last but not least, it is necessary to think about the historic buildings, such as churches, castles and palaces, statues, facades and roofs of buildings included in cultural heritage. For their protection and restoration are also spent considerable financial resources.

In fact, corrosion is a major financial problem (significant financial costs for repairs), whether in infrastructure, construction, mechanical engineering or cultural heritage, it also causes the failure rate and reduction in reliability of structural elements that can lead to serious consequences like property damage or the loss of life. It is good to know the atmospheric environment to which the materials are exposed, in order to eliminate any economic consequences. This article describes a method for creating a theoretical map of corrosion for basic construction materials according to EN ISO 9223, acquired from long term research in nearby European countries.

Long term research

Air Pollution Monitoring. Actually, from the commonly available literature, it is clear that in developed industrial countries in the late 19th century aggressivity of atmosphere rapidly began to increase. Air pollution not only causes health problems but also damage to historic buildings, monuments and ultimately the ecosystem. Environmental policy came to the forefront in the 80s of the 20th century. Convention on Long-range Transboundary Air was signed on 13 November 1979 in Geneva, leading to compliance with stricter criteria for industrial production. Those economic and environmental changes in many developed countries caused significant decreasing in concentration of SO_2 , and with it also the acidity of precipitation in the atmosphere. Degradation of materials in Europe caused by sulfur compounds is much lower today; despite the measures, air pollution is still a difficult problem, because many other factors causing increased corrosion loss of conventional materials are still used in human life [7-9]. It is important to constantly deal with effective strategies to reduce harmful substances in the air, side by side with the proposed solutions to solve the alarming climate of our planet.

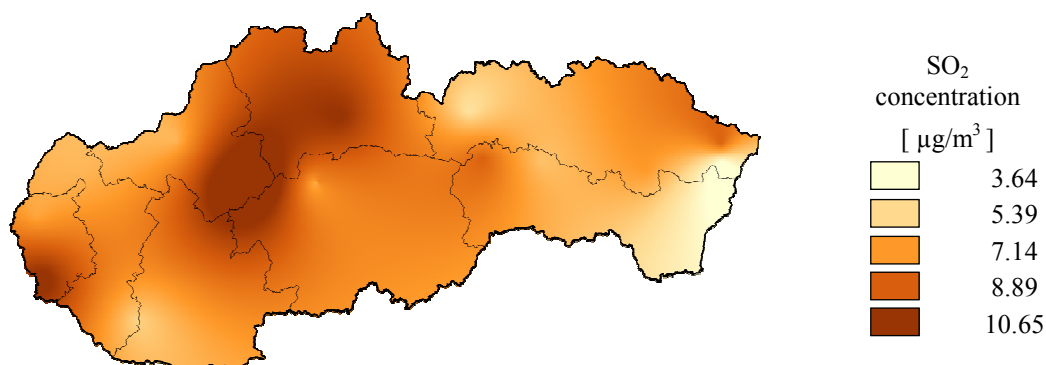


Fig. 1 Annual average of SO_2 concentration in atmosphere in Slovakia

Successfully established international agreements and protocols under the Convention on Long-range Transboundary Air lead to many scientific considerations. One of the International Co-operative Programs dealing with the influence of atmospheric pollutants on the degradation of various materials is ICP Materials, which, together with the European Monitoring Commission acts on the political level. The program was founded in 1985 in Stockholm and covers materials and cultural heritage [10]. The objective of this program is to quantitatively assess the impact of air multi-pollution, such as ozone, particulate matter, sulfur and nitrogen compounds and other substances, as well as evaluating parameters affecting atmospheric corrosion and pollution of major materials used in the construction and reconstruction of constructions and cultural heritage objects. Program intensively evaluates and describes the long-term corrosion to clarify the effect of pollutants on the environment and change of various materials. The results are used as a basis for

mapping areas with an increased risk of corrosion and contamination, and to calculate the cost incurred for damages caused by the degradation of materials.

Exposure Stations. In order to achieve long-term objectives, some short term objectives were formulated within the ICP Materials. It is primarily important to maintain and develop an international network of atmospheric corrosion exposure stations, evaluate the corrosion degradation and air pollution effects on materials exposed in the network of exposure stations, while collecting environmental data parameters in the vicinity of these stations.

Dose-response Functions. Based on long-term objectives dose-response functions were evolved, suitable for the calculation of maximum rate of corrosion, for the mapping of areas at increased risk of corrosion and to calculate the proportion attributable to air pollution. Given the obtained results could be at access to different materials and assess the impact of individual measured values of pollutants, it is possible to establish clear procedures of mapping areas with increased corrosion risk, facilitate mapping carried out by different institutions in different countries and develop new progressive materials or develop using of suitable materials. Some authors working on prediction of atmospheric corrosion using artificial neural network and developed more precise model compared to DRF [11].

Table 1 Dose-response functions of basic construction materials based on 8-year results from the exposure within ICP Materials (1987-1995) [16] and dose-response functions for basic construction materials based on 4-year results from the exposure within UN ECE ICP on Materials (1997-2001) [17].

Carbon steel:

$$ML = 29.1 + (21.7 + 1.39[SO_2]^{0.6}Rh_{60}e^{f(T)} + 1.29Rain[H^+] + 0.593PM_{10})t^{0.6} \quad (1)$$

$$f(T) = 0.15(T - 10), \text{ when } T < 10^\circ C; \text{ otherwise } f(T) = -0.054(T - 10)$$

Zinc:

$$ML_{8\text{-year}} = 1.4[SO_2]^{0.22}e^{0.018Rh}e^{f(T)}t^{0.85} + 0.029Rain[H^+]t \quad (2)$$

$$ML = 1.82 + (1.71 + 0.471[SO_2]^{0.22}e^{0.018Rh}e^{f(T)} + 0.041Rain[H^+] + 1.37[HNO_3])t \quad (3)$$

$$f(T) = 0.062(T - 10), \text{ when } T < 10^\circ C; \text{ otherwise } f(T) = -0.021(T - 10)$$

Copper:

$$ML_{8\text{-year}} = 0.0027[SO_2]^{0.32}[O_3]^{0.79}Rhe^{f(T)}t^{0.78} + 0.050Rain[H^+]t^{0.89} \quad (4)$$

$$ML = 3.12 + (1.09 + 0.00201[SO_2]^{0.4}[O_3]Rh_{60}e^{f(T)} + 0.0878Rain[H^+])t \quad (5)$$

$$f(T) = 0.083(T - 10), \text{ when } T < 10^\circ C; \text{ otherwise } f(T) = -0.032(T - 10)$$

Aluminum:

$$ML_{8\text{-year}} = 0.0021[SO_2]^{0.23}Rhe^{f(T)}t^{1.2} + 0.000023Rain[Cl^-]t \quad (6)$$

$$f(T) = 0.031(T - 10), \text{ when } T \leq 10^\circ C; \text{ otherwise } f(T) = -0.061(T - 10)$$

Results and Discussions

In the 50s of the 20th century within the CSSR was founded The State Research Institute of Materials Protection (SVÚOM), which was involved in research on metal corrosion problems and issues, surface treatment of various materials together with the Czechoslovak Academy of Sciences. Within this research were also founded the exposure stations in Slovakia. After the division of the CSSR, those corrosion exposure stations in Slovakia were abandoned. The Czech Republic actively participates in the program ICP Materials and result of this collaboration are also corrosion maps of standard and advanced structural materials [12-14] used in the transport infrastructure, power

industry and vehicles in Slovakia. The main objective is to establish a new corrosion exposure stations according to the standard EN ISO 8565 [15]. Those stations would be used for monitoring the effect of the air multi-pollution on the various materials, as well as the exposure of samples of each material in the free atmosphere, i.e. they would be directly exposed to all climatic conditions and air pollution.

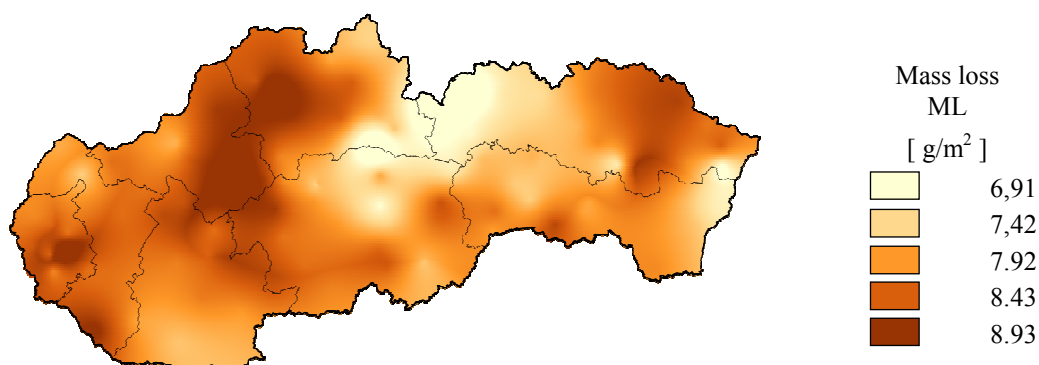


Fig. 2 Annual average mass loss of Zinc for the first year of exposure (Eq. 2)

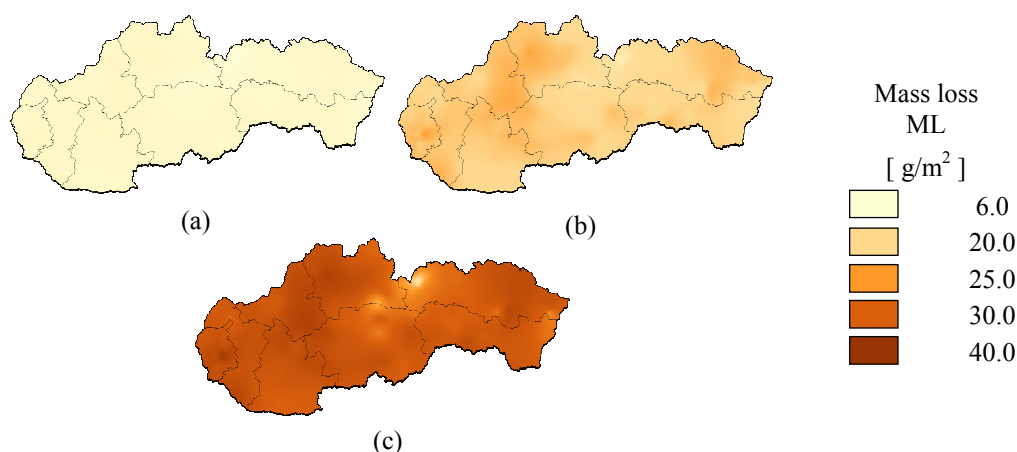


Fig. 3 Simulated mass loss of Zinc for: (a) first year of exposure; (b) three years of exposure; (c) five years of exposure (Eq. 2)

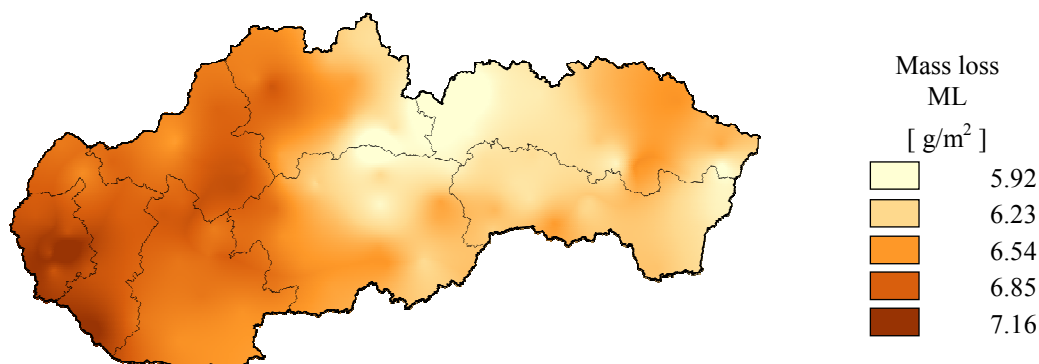


Fig. 4 Annual average mass loss of Zinc for the first year of exposure (Eq. 3)

Actually, based on the dose-response functions, which were the result of 8 years of research in the exposure of the ICP Materials in some European countries (Sweden, Norway, Italy, Czech Republic, Switzerland, France, Great Britain, Germany, Austria) in 1987 - 1995 (Table 1) and depending on the amount of data pollution and climatological conditions provided by the Slovak

Hydro meteorological Institute (SHMÚ) maps were interpolated of weight loss for basic construction materials in Slovakia (zinc, copper, carbon steel, aluminum). Figure 2 and Figure 3 show the preliminary maps of zinc weight loss prepared according to dose-response function (Eq. 2). Some dose-response functions were affected by nitrogen compounds in the period 1997-2001 (Table 1), that result for zinc (Eq. 3) was again used to create approximate maps of zinc weight losses (Fig. 4, Fig. 5). In the years 2002-2003, the further research should take into account only the one year of exposure materials, so the dose-response functions do not indicate the time value (Table 2). From the last equation for zinc (Eq. 8) a corrosion map rate in μm , shown in figure 6, was created.

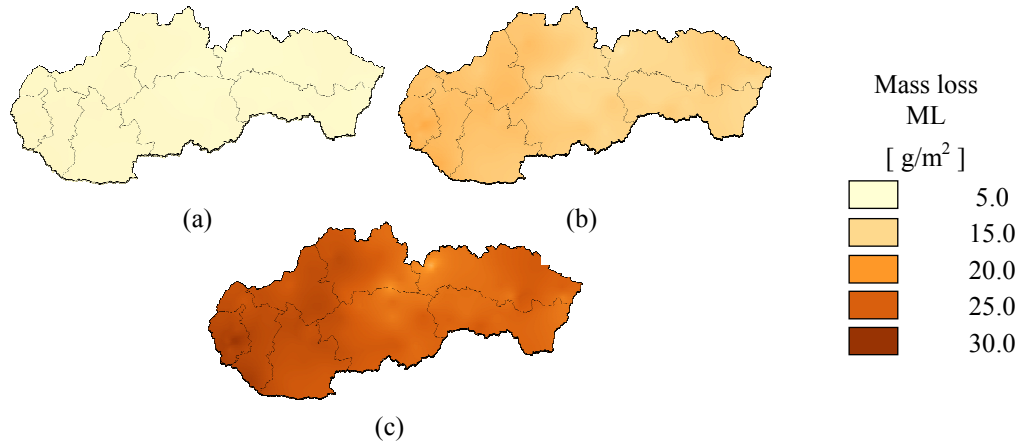


Fig. 5 Simulated mass loss of Zinc for: (a) first year of exposure; (b) three years of exposure; (c) five years of exposure (Eq. 3)

Table 2 Dose-response functions of basic construction materials based on 4-year results from the exposure within UN ECE ICP on Materials (1997-2001) completed with environmental measurements of HNO_3 and particulate matter (2002-2003) [18].

Carbon steel:

$$R = 6.5 + 0.178[\text{SO}_2]^{0.6}\text{Rh}_{60}\text{e}^{f(T)} + 0.166\text{Rain}[\text{H}^+] + 0.076\text{PM}_{10} \quad (7)$$

$$f(T) = 0.15(T - 10), \text{ when } T < 10^\circ\text{C}; \text{ otherwise } f(T) = -0.054(T - 10)$$

Zinc:

$$R = 0.49 + 0.066[\text{SO}_2]^{0.22}\text{e}^{0.018\text{Rh} + f(T)} + 0.0057\text{Rain}[\text{H}^+] + 0.192[\text{HNO}_3] \quad (8)$$

$$f(T) = 0.062(T - 10), \text{ when } T < 10^\circ\text{C}; \text{ otherwise } f(T) = -0.021(T - 10)$$

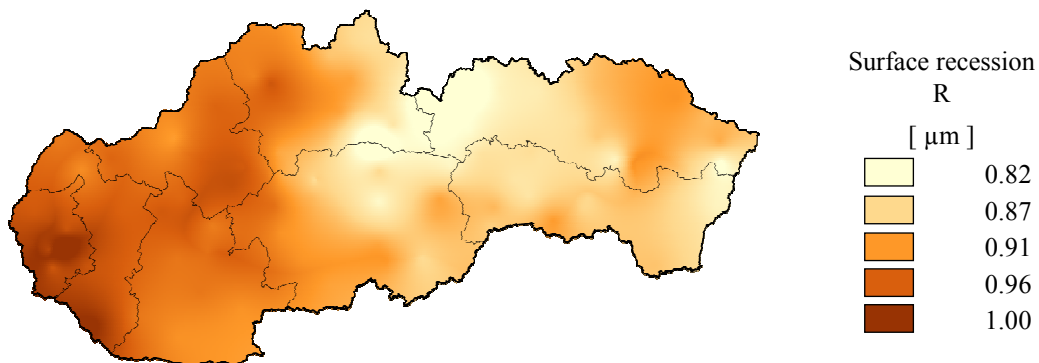


Fig. 6 Annual average surface recession of Zinc for the first year of exposure (Eq. 8)

STN ISO 9223 September 1995 expired and was replaced by EN ISO 9223 in July 2012. This international standard specifies a system of classification of corrosion of atmospheric aggressivity and also defines the dose-response functions for standard metals (Table 3), which are needed for estimation of corrosion aggressivity based on corrosion decrease for the first year of exposure. For comparison a map of corrosion rate of zinc was interpolated (Fig. 7), according to equation (Eq. 10).

Table 3 Dose-response functions for construction materials based on results from the exposure defined by EN ISO 9223 (2012) [19].

Carbon steel:

$$r_{\text{corr}} = 1.77P_d^{0.52}e(0.020Rh + f_{\text{St}}) + 0.102S_d^{0.62}e(0.33Rh + 0.04T) \quad (9)$$

$$f_{\text{St}} = 0.150(T - 10), \text{ when } T \leq 10^\circ\text{C}; \text{ otherwise } -0.054(T - 10)$$

Zinc:

$$r_{\text{corr}} = 0.0129P_d^{0.44}e(0.046Rh + f_{\text{Zn}}) + 0.0175S_d^{0.57}e(0.008Rh + 0.085T) \quad (10)$$

$$f_{\text{Zn}} = 0.038(T - 10), \text{ when } T \leq 10^\circ\text{C}; \text{ otherwise } -0.071(T - 10)$$

Copper:

$$r_{\text{corr}} = 0.0053P_d^{0.26}e(0.059Rh + f_{\text{Cu}}) + 0.01025S_d^{0.27}e(0.036Rh + 0.049T) \quad (11)$$

$$f_{\text{Cu}} = 0.126(T - 10), \text{ when } T \leq 10^\circ\text{C}; \text{ otherwise } -0.080(T - 10)$$

Aluminum:

$$r_{\text{corr}} = 0.0042P_d^{0.73}e(0.025Rh + f_{\text{Al}}) + 0.0018S_d^{0.60}e(0.020Rh + 0.094T) \quad (12)$$

$$f_{\text{Al}} = 0.009(T - 10), \text{ when } T \leq 10^\circ\text{C}; \text{ otherwise } -0.043(T - 10)$$

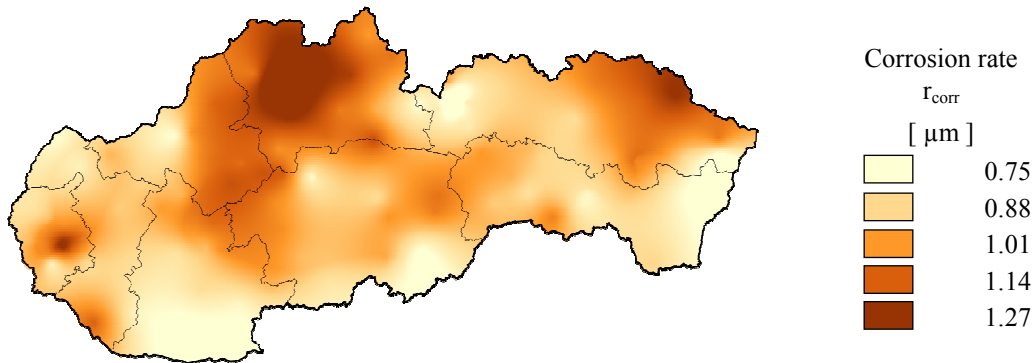


Fig. 7 Annual average corrosion rate of Zinc for the first year of exposure (Eq. 10)

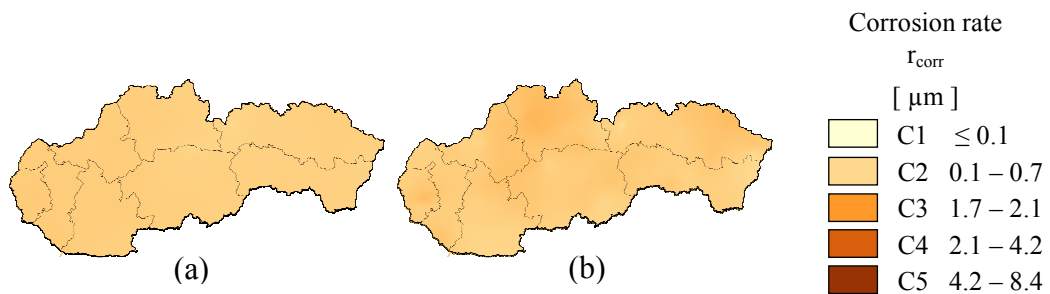


Fig. 8 Corrosivity categories for the atmospheric environments by the first-year corrosion rate of Zinc: (a) equation (8); (b) equation (10)

Table 4 Parameters used in the dose-response functions

Abbreviation	Parameter description	Unit	Abbreviation	Parameter description	Unit
t	Time	Years	[O ₃]	O ₃ concentration	μg.m ⁻³
T	Temperature	°C	PM ₁₀	PM concentration (<10μm)	μg.m ⁻³
Rh	Relative humidity	%	ML	Mass loss	g.m ⁻²
Rain	Amount of precipitation	mm year ⁻¹	R	Surface recession	μm
[H ⁺]	Acidity of precipitation	mg.l ⁻¹	r _{corr}	Surface recession	μm
[SO ₂]	SO ₂ concentration	μg.m ⁻³	P _d	SO ₂ deposition	mg/(m ² .year)
[Cl ⁻]	Cl ⁻ concentration	μg.m ⁻³	S _d	Cl ⁻ deposition	mg/(m ² .year)
[HNO ₃]	HNO ₃ concentration	μg.m ⁻³			

Conclusion

In fact, establishing of the atmospheric corrosion exposure stations in Slovakia according to the standard EN ISO 8565 is related to the preparation of samples served for measurement of surface degradation and surface layers, including volumes of conventional and advanced structural materials under realistic conditions, as well as control samples and reference. It is also necessary to propose place for exposure racks with samples, depending on the type of atmosphere, classified by EN ISO 9223 - urban, rural and industrial. To evaluate the results of the corrosion tests, it is necessary to characterize the atmospheric conditions at the exposure station. Therefore, the importance of cooperation with the SHMÚ is necessary and the location of the corrosion exposure stations near their stations is perspective because of climatological and air multi pollutant data-recording.

When creating the final product, *corrosion map* for construction materials cooperation will be required with experts in the area of meteorology focusing on detection of pollutants in the atmosphere, as measured values of air pollution are relatively unstable and quantity of measuring stations, given the size and diversity of the Slovak relief is very low.

In accordance with the climate and air pollution in Slovakia will be a long term objective to design and modify dose-response functions for individual construction materials, to focus the impact not only of sulfur, nitrogen, carbon, particles matter, ozone, but also on the impact of UV radiation and chloride content, not only in air or in precipitation, in general, but also focusing on areas close to the network of roads, especially bridge structures.

Acknowledgment:

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References

- [1] B. Hadzima, T. Liptáková, Fundamentals of electrochemical corrosion of metals, University of Žilina, Žilina, 2008. (in Slovak)
- [2] M. Černý, The corrosion properties of metallic structural materials, STNL Praha, Praha, 1984. (in Czech)
- [3] T. Liptáková, I. Šestina, Fundamentals of corrosion and protection of metals in the gas industry, University of Žilina, Žilina, 1997. (in Slovak)
- [4] M.G. Fontana, Materials science and engineering, McGraw-Hill, Inc., New York, 1986.
- [5] J.P. Broomfield, Corrosion of steel in concrete, E & FN SPON, London, 1997.

- [6] P. Pullar-Strecker, Corrosion Damaged Concrete, CIRIA, London, 1987.
- [7] K. Kreislová, A. Koukalová, D. Knotková, Trends of corrosivity of the atmosphere and the corrosion loss of zinc in atmospheric conditions, The corrosion and protection of material, 5 (2011) 19-22. (in Czech)
- [8] K. Kreislová, A. Koukalová, T. Laník, K. Hovorková, The life of the zinc coating on the construction of traffic infrastructure, Proceedings of the 17th Conference of hot-dip galvanizing, Ostrava, 2011, pp. 39-44. (in Czech)
- [9] D. Knotková, K. Kreislová, The corrosion behavior of metals and metal coatings in an atmospheric environment, SVÚOM Praha, 2010. (in Czech)
- [10] Information on <http://www.corr-institute.se/ICP-Materials/web/page.aspx?sid=3293>
- [11] M. Halama, K. Kreislová, J.V. Lysebettens, Prediction of Atmospheric Corrosion of Carbon Steel Using Artificial Neural Network Model in Local Geographical Regions, Corrosion: The Journal of Science and Engineering. Vol. 67, 6 (2011), 1-6.
- [12] K. Kreislová, D. Knotková, I. Skořepová, Corrosion map of CZ for zinc, SVÚOM Praha, 2009. (in Czech)
- [13] K. Kreislová, D. Knotková, I. Skořepová, Corrosion map of CZ for carbon steel, SVÚOM Praha, 2009. (in Czech)
- [14] K. Kreislová, D. Knotková, I. Skořepová, Corrosion map of CZ for copper, SVÚOM Praha, 2009. (in Czech)
- [15] STN EN ISO 8565 Metals and alloys - Atmospheric corrosion testing - General requirements, SUTN, (2011).
- [16] J. Tidblad, V. Kučera, A.A. Mikhailov, J. Henriksen, K. Kreislová, T. Yates, B. Stöckle, M. Schreiner, UN/ECE ICP Materials: Dose-response functions on dry and wet acid deposition effects after 8 years of exposure, Netherlands, 2001, pp.1458-1462.
- [17] Information on <http://www.corr-institute.se/MULTI-ASSESS>
- [18] T. Spranger, U. Lorenz, H.-D. Gregor, Manual on methodologies and criteria for Modelling and Mapping Critical Loads & Levels and Air Pollution Effects, Risks and Trends, Umweltbundesamt, Berlin, 2004.
- [19] STN EN ISO 9223 Corrosion of metals and alloys - Corrosivity of atmospheres - Classification, determination and estimation, SUTN, (2012).

IV. Surface Treatment

Influence of anodic oxidation on the polarization resistance of Ti6Al4V alloy after shot peening

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Keywords: Ti6Al4V alloy, anodic oxidation, shot peening, EIS, corrosion

Abstract. Ti6Al4V titanium alloy is widely used for industrial and medical applications. Several techniques of surface treatment are used to improve their mechanical, fatigue or corrosion properties like shot peening or anodic oxidation. The effect of these techniques combination on corrosion resistance of the base material was examined in this study. For this purpose, electrochemical impedance spectroscopy tests were performed in 0.1M NaCl solution. Shot peening was carried out using ceramic balls Z850 (Φ 850 μ m) at the Almen intensity of 0.13 mmA. Anodic oxidation process was performed on ground and shot peened surface in 7% H₂SO₄ acid solution at constant used voltage of 65 V. Significant improvement of corrosion resistance by the surface treatment of Ti6Al4V alloy by shot peening with following anodic oxidation was observed however the improvement was lower when compared to surface treated only by anodic oxidation.

Introduction

Ti6Al4V is one of the most used ($\alpha+\beta$) titanium alloys. Ti6Al4V can be due to the good mechanical properties and corrosion resistance used for many applications, such as transportation, aerospace industry, power industry and it is also useful for the medical applications [2,3]. The reasons for the use of this alloy are high strength and ductility [1]. The excellent corrosion resistance of titanium is attributed to the formation of protective oxide film formed on the metal surface in contact with air. But this natural oxide film is poor and thin having a thickness of 3–5 nm. Therefore, despite its high corrosion resistance in normal conditions, the natural oxide film exhibits poor tribological and tribocorrosion properties [3].

In order to overcome this problem, several surface modification techniques have been used to improve the corrosion and wear resistance of titanium alloys. These include thermal oxidation, ion implantation, plasma spray and anodic oxidation [4]. Anodic oxidation is a simple and effective technique allowing to enlarge the thickness of TiO₂ oxide layer thus improving corrosion and wear properties of the surface [5].

Next conventional technique improving fatigue strength, hardness, fretting fatigue resistance and abrasion resistance of titanium alloys is shot peening [6]. Shot peening is a method of cold working in which compressive residual stresses are induced in the exposed surface layers of metallic parts by the impingement of stream of shots, directed at the metal surface at high velocity under controlled conditions [7].

The effect of combination of shot peening and anodic oxidation on corrosion properties was studied on 2024 Al alloy [8] with successful results, but there are no similar studies performed on Ti alloys although these techniques are separately well investigated. For these reasons, this paper is

focused on the investigation of corrosion resistance of Ti6Al4V alloy treated by shot peening followed by anodic oxidation and comparison with individually treated surface.

Experimental material

Ti6Al4V titanium alloy was used in this study as an experimental material. It was delivered in hot rolled state after heat treatment at 730°C / 1 hour. Chemical composition of the examined material is given in Table 1. The microstructure of tested alloy is bimodal (Fig. 1). It consists of elongated grains of α phase (white grains) with average grain size of 6.5 μm and β phase (gray grains) with average size of 4.8 μm .

Table 1 Chemical composition of Ti6Al4V (wt. %) [9].

N	C	Fe	O	Al	V	Ti
0.003	0.026	0.190	0.177	6.43	4.07	rest



Fig. 1 Microstructure of tested Ti6Al4V alloy, etch. 10 ml HF, 5 ml HNO₃ and 85 ml H₂O

Experimental methods

Grinding on P500 emery paper followed by rinsing in demineralized water and hot air streaming was used as a pretreatment process before shot peening and anodic oxidation.

Shot peening (SP) was performed on flat ground samples using ceramic balls Z850 (Φ 850 μm) with Almen intensity of 0.13 mmA. It was followed by air streaming and ultrasonic cleaning in demineralized water and ethanol in order to remove impurities from shot peening process.

Anodic oxidation was carried out on ground surface and on the surface that was shot peened. The electrolyte used for the treatment was the solution of 7% of H₂SO₄ acid. Voltage of 65V was used for the treatment at the temperature of 12 °C and time 20 min [10].

For the corrosion resistance measurements four batches of Ti6Al4V samples with different surface treatment were used. As a basic material samples with only ground surface were used. Then samples with surface treated only by shot peening or anodic oxidation were used. As a main sample batch for this study corrosion resistance of the samples with surface treated by combination of shot peening with anodic oxidation was examined.

The corrosion resistance of particular treated samples of Ti6Al4V alloy was evaluated by electrochemical impedance spectroscopy (EIS). All the corrosion experiments were performed at 22 $\pm$ 1 °C in 0.1M NaCl solution simulating aggressive sea atmosphere. Stabilization time of open circuit potential after immersion of the sample into electrolyte was 15 minutes. Measurements were

performed at open circuit potential with AC voltage amplitude of 15 mV in frequency range from 100 kHz to 1 mHz.

Results and discussion

Based on the EIS measurements on treated Ti6Al4V samples the values of polarization resistance R_p , expressing the corrosion resistance of the surface layer or layers, can be calculated from the measured Nyquist diagrams (Fig. 2). These obtained R_p values are given in Table 2.

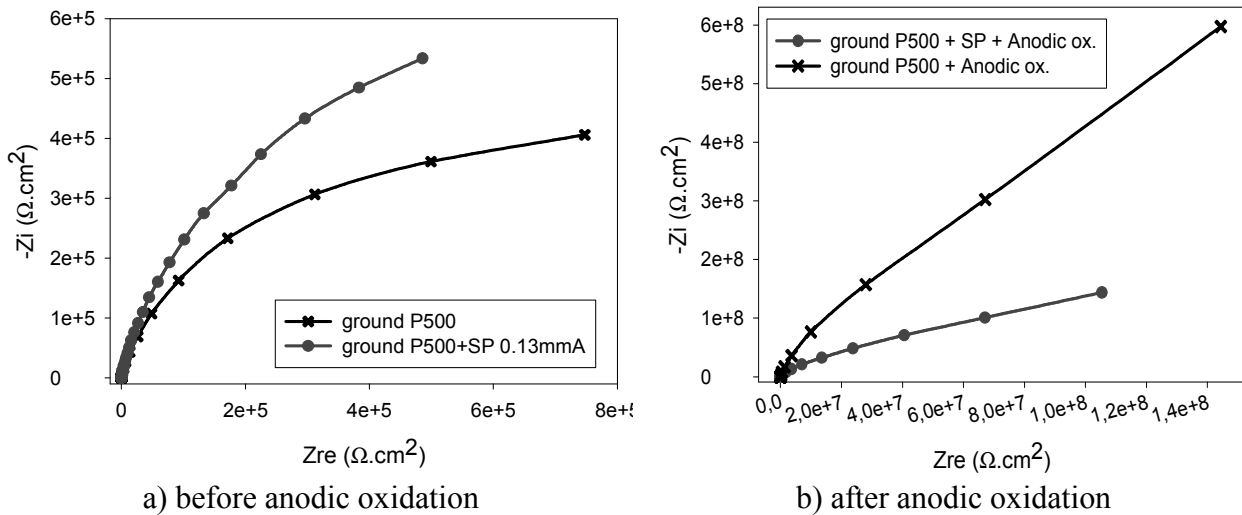


Fig. 2 Nyquist diagrams of Ti6Al4V samples after various surface treatments (0.1M NaCl)

Table 2 Polarization resistance R_p of Ti6Al4V alloy samples after various surface treatments

Surface treatment	Grinding	Grinding + SP	Grinding + SP + Anodic oxidation	Grinding + Anodic oxidation
R_p [$M\Omega \cdot cm^2$]	1.1	1.4	1009.2	8821.4

Polarization resistance values show, the surface treatment of Ti6Al4V alloy by shot peening and by anodic oxidation also improved the corrosion resistance of the base material. R_p increase caused by SP under specified conditions was merely slight (from 1.1 $M\Omega \cdot cm^2$ for the ground material to 1.4 $M\Omega \cdot cm^2$ for surface treated by SP). This positive effect of SP on corrosion properties of the base material was caused by intensive plastic deformation of the surface by shot peening medium. Increased inner energy in near surface area generated more favorable conditions for proper creation of TiO_2 natural oxide on the samples surface.

Anodic oxidation performed on shot peened surface achieved massive increase of polarization resistance values about 3 orders of magnitude (1.1 $M\Omega \cdot cm^2$ for ground surface compared to 1009.2 $M\Omega \cdot cm^2$ for surface treated by shot peening and anodic oxidation). This proved that shot peened surface enables the production of thicker and more compact TiO_2 surface oxide layer by anodic oxidation what is very positive finding in terms of corrosion.

However, the pretreatment by SP did not ensure the better conditions for process of anodic oxidation in order to reach better corrosion resistance when compared to the surface prepared only by grinding. This was revealed by almost 9-fold lower value of R_p compared to ground samples treated by anodic oxidation. This finding could be misleading, because the used parameters of anodic oxidation were the same for ground surface and for shot peened surface also. It is necessary to take into consideration that surface properties, potential and other parameters of shot peened

surface are different from the ground surface. Thus, separate individual research focused on optimization of anodic oxidation parameters on a shot peened surface is necessary in order to maximize the quality of formed TiO₂ oxide layer and its corrosion and wear resistance.

Conclusions

On the basis of performed experiments can be concluded the following:

- the highest value of the polarization resistance R_p was measured on the ground samples treated by anodic oxidation in 7 % H₂SO₄ solution for 20 minutes,
- shot peening by ceramic balls at 0.13 mmA slightly improved the corrosion resistance of the Ti6Al4V alloy when compared to surface ground with P500 emery paper,
- shot peening and following anodic oxidation of ground surface significantly improved the corrosion resistance of Ti6Al4V alloy samples.

Acknowledgments

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Literature References

- [1] E. Vasilescu, P. Drob, D. Raducanu, I. Cinca, D. Mareci, J.M. Calderon Moreno, M. Popa, C. Vasilescu, J.C. Mirza Rosca, Effect of thermo-mechanical processing on the corrosion resistance of Ti6Al4V alloys in biofluids, *Corr. Sci.* 51 (2009) 2885–2896.
- [2] E. Vermesse, C. Mabru, L. Arurault, Surface integrity after pickling and anodization of Ti–6Al–4V titanium alloy, *Appl. Surf. Sci.* 285P (2013) 629–637.
- [3] M. Janecek, F. Nový, J. Stráský, P. Harcuba, L. Wagner, Fatigue endurance of Ti-6Al-4V alloy with electro-eroded surface for improved bone in-growth, *J. of the Mech. Behav. of Biomed. Mater.* 4 (2011) 417–422.
- [4] M.R. Garsivaz jazi, M.A. Golozar, K. Raeissi, M. Fazel, Evaluation of corrosion and tribocorrosion of plasma electrolytic oxidation treated Ti–6Al–4V alloy, *Surf. & Coat. Technol.* 244 (2014) 29–36.
- [5] H. Lukáčová, B. Plešingerová, M. Vojtko, G. Bán, Electrochemical treatment of Ti6Al4V, *Acta Metallurgica Slovaca* 16 (2010) 186–193.
- [6] G.Q. Chen, Y. Jiao, T.Y. Tian, X.H. Zhang, Z.Q. Li, W.L. Zhou, Effect of wet shot peening on Ti–6Al–4V alloy treated by ceramic beads, *Trans. Nonferrous Met. Soc. China* 24 (2014) 690–696.
- [7] B.K.C. Ganesh, W. Sha, N. Ramanaiah, A. Krishnaiah, Effect of shot peening on sliding wear and tensile behavior of titanium implant alloys, *Materials and Design* 56 (2014) 480–486.
- [8] D.T. Asquith, A.L. Yerokhin, J.R. Yates, A. Matthews, The effect of combined shot-peening and PEO treatment on the corrosion performance of 2024 Al alloy, *Thin Solid Films* 516 (2007) 417–421.
- [9] L. Škublová, B. Hadzima, L. Borbás, M. Vitosová: *Mater. Eng.-Mater. Inž.* 15(4) (2008) 18–22.
- [10] Z.M. Yan, T.W. Guo, H.B. Pan, J.J. Yu, Influences of Electrolyzing Voltage on Chromatics of Anodized Titanium Dentures, *Mater. Trans.* 43(12) (2002) 3142–3145.

Quality Evaluation of HVOF Coatings on the Basis of WC-Co in Tribocorrosive Conditions

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Keywords: HVOF coating, boron nitride, wear, corrosion.

Abstract. Article deals with analysis of production and characteristics of ceramic coatings applied using HVOF technology. It presents the results of research focused on quality evaluation of HVOF coatings on the basis of WC-Co and impact of Boron Nitride protective layer. HVOF coatings were exposed to hard tribocorrosive conditions. For determining of corrosive resistance of coatings 1M solution of NaCl, potentiodynamic tests and accelerated salt spray test were used. Experiment confirmed that using of Boron Nitride protective coating clearly improves corrosive resistance of the coating on the basis of WC-Co even in hard combined tribocorrosive conditions. Protective layer seals the pores in the structure of coating and thus prevents the formation of corrosion and subsequent depreciation of coating in various corrosive environments. Using of protective layer thus improves lifetime and reliability of spraying and the part itself. Improved lifetime positively influences also the economics of the operation of energetic equipment in which these coating are used.

Introduction

HVOF coatings are very hard metallic or hard particle-metallic binder functional coatings with very good corrosion resistance. However, porosity of thermal spray coatings can lead to decreasing their corrosion resistance in critical applications such as sink rolls in molten zinc. Sealing the thermally sprayed coatings can minimise their porosity from 1–2% to zero, therefore preventing the corrosive agents from penetrating to the substrate material. Sealing can either be done with different sealants, which are applied by painting onto the substrate, closing the open porosity of the coating surface, or by laser treatment [1]. In laser treatment, a thin surface of the coating is melted and resolidified into a compact, homogeneous, nonporous layer [2]. The morphology and composition of the laser treated cladding are transformed from the original sprayed structure [3]. Applying sealing agent increases the cost of the coating, however, if the protective effect of the sealant is long enough, it can be economically applied for critical mechanical parts subject to corrosion.

The paper deals with results of research focused on the influence of sealing boron nitride on corrosion resistance and wear of coating WC-Co (Amperit 512.074).

Materials and Methods

In experimental part there was evaluated coating formed using WC-Co powder (88/12). WC-Co 88/12 powder (agglomerated sintered) is a special product for applications where coated parts are exposed to molten non-ferrous metals such as Zn and Galfan used in continuous galvanizing lines. It has been specifically developed for deposition by HVOF systems. Sprayed coatings are low in porosity providing effective substrate protection. Provides higher corrosion resistance against liquid

metals compared to normal WC-Co grades. Chemistry characteristics of powder (in mass %): C max. 4, Co 10-12, W balance. Particle size 15-45 μm . Spraying parameters for JP-5000 spraying equipment: nozzle – 4 inch, Kerosene 22,7 l/h, Oxygen 792 nl/min, feed rate 75 g/min, stand-off 380 mm.

Studied coating was applied on the base material of grade STN 412020 (C15E). The test samples had a cylindrical shape with a diameter of 25 mm and a length of 50 mm. Coating was applied on the base of the cylinder. The surface of the base material was blasted before spraying by white corundum with grain size of 0.7 mm, air pressure 0.4 MPa, stand-off 300 mm, impact angle of 90 °. One group of coatings have been investigated as-sprayed (A), on the coating's surface of the second group (B) was applied the sealing - boron nitride.

Structure, composition and thickness of the coating was studied on metallographic sections using SEM. The hardness of the coating was determined using test equipment Shimadzu HMV-2E with a load of 980.7 mN (HV 0.1), hold time 15 seconds.

The corrosion rate of the coating was determined by Tafel analysis using test device Potentiostat SP150 [4]. The corrosion rate depends on the kinetics of both anodic (oxidation) and cathodic (reduction) reactions [5,6]. According to Faraday's law, there is a linear relationship between the metal dissolution rate or corrosion rate, i_{corr} (1):

$$R_M = \frac{M}{\eta F \rho} i_{\text{corr}} \quad (1)$$

where M is the atomic weight of the metal, ρ is the density, η is the charge number which indicates the number of electrons exchanged in the dissolution reaction and F is the Faraday constant, (96.485 C/mol). The ratio M/η is also sometime referred to as equivalent weight.

Calculation of corrosion rates requires the determination of corrosion currents. When reaction mechanisms for the corrosion reaction are known, the corrosion currents can be calculated using Tafel Slope Analysis. The relationship between current density and potential of anodic and cathodic electrode reactions under charge transfer control is given by the Butler-Volmer equation (2), (3):

$$i = i_{\text{corr}} \left(e^{2.303 \frac{\eta}{b_a}} - e^{2.303 \frac{\eta}{b_c}} \right) \quad (2)$$

$$\eta = E - E_{\text{corr}} \quad (3)$$

where E is the applied potential and i the measured current density. The overpotential, η , is defined as the difference between applied potential and the corrosion potential E_{corr} . The corrosion potential, E_{corr} is the open circuit potential of a corroding metal. The corrosion current, i_{corr} , and the Tafel constants b_a , and b_c can be measured from the experimental data. For large anodic overpotentials ($\eta/b_a \gg 1$) the Butler-Volmer equation simplifies to the Tafel equation for the anodic reaction (4):

$$\eta = \log(i_{\text{corr}}) + b_a \cdot \log(i) \quad (4)$$

Analogously, for large cathodic overpotentials ($\eta/b_c \ll -1$) the Tafel equation for the cathodic reaction is given by (5):

$$\eta = \log(i_{\text{corr}}) + b_c \cdot \log |i| \quad (5)$$

The Tafel equations predict a straight line for the variation of the logarithm of current density with potential.

Unsealed coating (A) was investigated under parameters for WC and sealed coating (B) under parameters for boron nitride. Tafel analysis was performed in 3.5% NaCl solution. Used parameters summarizes Table 1.

Tab. 1 Parameters used in Tafel analysis of the coating

	A	B
equivalent weight	195,851 g/eq.	24,820 g/eq.
density	15,630 g/cm ³	3,450 g/cm ³
surface area	0,636 cm ²	0,636 cm ²

Tribological properties of the coating were determined by the pin-on-disc under the normal load of 1.5 N, a speed of 0.02 ms⁻¹, static counterpart was WC ball with a diameter of 6 mm. Duration of test was 1 hour and was carried out in 1M NaCl solution.

Results

Microstructure of the coating is shown in Fig. 1

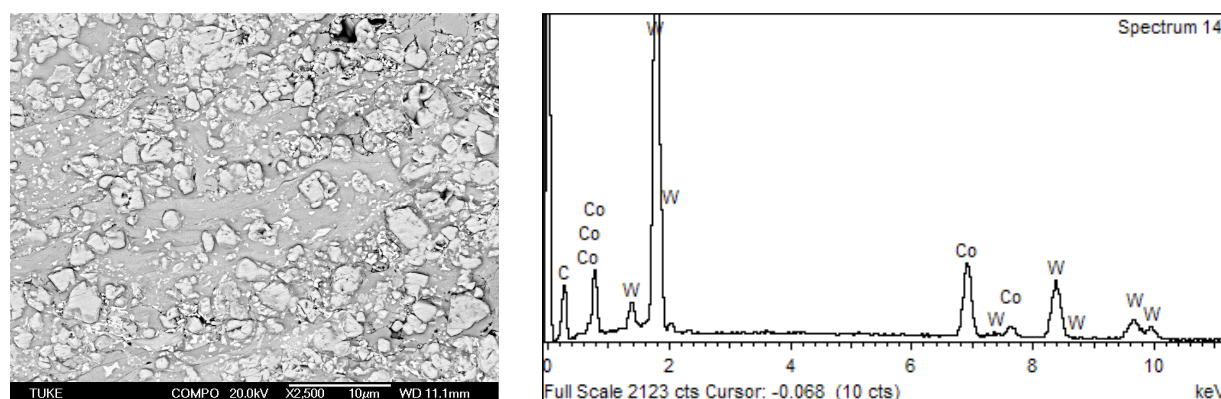


Fig. 1 Structure and EDX analysis of the WC-Co coating

Fig. 1 shows that the coating consists of hard WC particles, which are surrounded by binding matrix of Co. Size of WC particles is up to 5 μm and are evenly spaced in the Co matrix. EDX analysis confirms the presence of the essential building elements in the coating. The average thickness of the coating observed on metallographic sections is 136 μm . Microhardness of the base material is 168 HV 0.1, and of the coating 1247 HV 0.1. Results of Tafel analysis are shown in Table 2.

Tab. 2 Measured corrosion values

	A	B
(x) E _{corr}	- 740,117 mV vs. SCE	-697,775 mV vs. SCE
(x) I _{corr}	10,900 μA	3,848 μA
(x) b _c	110,1 mV	85,9 mV
(x) b _a	200,0 mV	137,7 mV
χ^2	69,767 5	2 046,04
corrosion rate	0,702 667 mmpy	0,142 421 mmpy

The corrosion rate of the unsealed WC-Co coating was 0.7 mm/year, application of sealant boron nitride led to decreasing of coating corrosion rate to 0.14 mm/year. The results of the pin-on-disc test - coefficient of friction and the mass loss of the coating are shown in Fig. 2 and Table 3.

Tab. 3 Mass loss of the coating

coating	Initial weight [g]	Weight after wear test [g]	Weight change [g]
A	18,3345	18,3352	+ 0,0007
B	19,2288	19,2226	- 0,0062

For unsealed coating was observed weight gain, which was probably caused by NaCl penetration into the pores in the coating structure. For sealed coating was found weight loss of the coating.

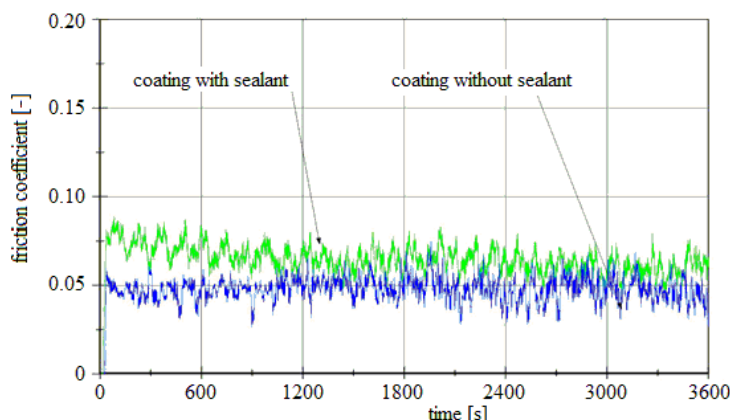


Fig. 2 Course of friction coefficient of the coating

Conclusions

Based on the experiment it can be concluded that the use of Boron Nitride sealant increases the corrosion resistance of coatings based on WC-Co even in harsh combined tribocorrosive conditions. Protective boron nitride seals the pores in the structure of the HVOF coating and thereby prevents corrosion and subsequent degradation of the coating in various corrosive environments. Use the protective boron nitride layer so extends the life and reliability as of the HVOF coating as of the mechanical part itself. Prolonged life has a positive impact on the economy of operation of equipment with HVOF coatings.

Acknowledgement

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References

- [1] M. Oksa, E. Turunen, T. Varis, Sealing of thermally sprayed coatings, *Surf. Eng.* 20 (2004) 251-254.
- [2] J. Tuominen, P. Vouristo, T. Mäntylä, S. Ahmaniemi, J. Vihinen, P.H. Andersson, Corrosion Properties of HVOF Sprayed and Nd-YAG Laser Remelted High-Chromium Nickel-Chromium Coatings, in: C.C. Berndt, K.A. Khor, E.F. Lugscheider (Eds.), *Thermal spray 2001: new surfaces for a new millennium, 2001*; Materials Park, OH, ASM International.
- [3] P. Serra, J.M. Miguel, J.L. Morenza, J.M. Guilemany, Structural characterization of laser-treated $\text{Cr}_3\text{C}_2\text{-NiCr}$ coatings, *J. Mater. Res.*, 16 (2001) 3416–3422.
- [4] Metrohm, Autolab B.V., Corrosion: Part 2 – Measurement of Corrosion Rates , [cit 2014-6-30]. Available on the internet: http://www.ecochemie.nl/download/Applicationnotes/Autolab_Application_Note_COR02.pdf
- [5] J. Vrátná, B. Hadzima, M. Bukovina, M. Janecek, Room temperature corrosion properties of AZ31 magnesium alloy processed by extrusion and equal channel angular pressing, *J. Mater. Sci.* 48 (2013) 4510-4516.
- [6] L. Bukovinova, B. Hadzima, Electrochemical characteristics of magnesium alloy AZ31 in Hank's solution, *Corr. Eng. Sci. Technol.* 47 (2012) 352-357.

Effect of surface treatment by DCPD coating on corrosion resistance of magnesium alloy Elektron 21

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Keywords: magnesium alloys, electrodeposition, corrosion resistance, electrochemical properties, dicalcium phosphate dehydrate

Abstract. Electrodeposition process of calcium phosphate (CaP) was performed on Elektron 21 magnesium alloy and the influence on corrosion resistance of the alloy covered by CaP was investigated by electrochemical tests. The electrodeposition treatment was performed by potential controlled method in water solution consisting of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$ and H_2O_2 . Corrosion measurements were performed in 0.1M NaCl solution at laboratory temperature (22 ± 1 °C) using electrochemical impedance spectroscopy. Electrodeposited surfaces had higher polarization resistance than only ground surface after all exposition time in 0.1M NaCl.

Introduction

Magnesium alloys become more and more used in modern industry, due to their excellent strength/density ratio, making them in many cases attractive in strategic sectors such as the transport and power industry. Moreover, many technological problems have been overcome, allowing the employment of some magnesium alloys also at relatively high temperatures. In particular, alloys containing elements of the rare-earths (RE) have been the object of intensive studies, both for technological applications and for scientific investigations [1,2,3].

Elektron 21 is new magnesium based casting alloy containing rare elements (Nd and Gd) for aerospace application up to the 200°C. It has high strength, good corrosion resistance and excellent castability. Specifically, the EV31 alloy (formerly known as Elektron 21) has been introduced to special applications as substitute of the most known WE43 alloy, due to its improved corrosion resistance and reduced production costs [4]. One of the major disadvantages of Mg is the value of the standard potential (-2.36 V), which leads to high electrochemical reactivity and low corrosion resistance. Therefore, considerable efforts lead to development of the new type of Mg alloys and optimization of technology process [5,6,7,8].

Aim of this study is evaluation of electrochemical properties of Elektron 21 magnesium alloy surface in 0.1M NaCl after grinding and after grinding followed by electrodeposition of calcium phosphate layer.

Experimental material

An extruded magnesium alloy, Elektron 21, was examined. The alloy was purchased from Magnesium - Electron, Manchester, UK. The alloy's chemical composition is given in Table 1. Microstructural investigation was performed by CARL ZEISS AXIO Imager.A1m light metallographic microscope using AxionVision Rel 4.5 software and AxioCam MRc5. The samples for metallographic observation were prepared by conventional metallographic procedures. For visualization of the magnesium alloy microstructure, etchant consisted of 0.5 % nital was used. The microstructure of the extruded sample (Fig. 1) is formed by polyedric grains of supersaturated solution of zirconium, RE and other alloying elements in magnesium. Areas of the Mg_{12}Nd intermetallic phase are visible in the microstructure [9]. The average grain size is 14 μm .

Table 1 Chemical composition of tested Mg alloy

Component	Nd	Gd	Zr	Fe	Cu	Ni	Zn	Mg
wt. %	2.90	1.3	0.32	0.002	0.001	<0.0005	0.32	balance

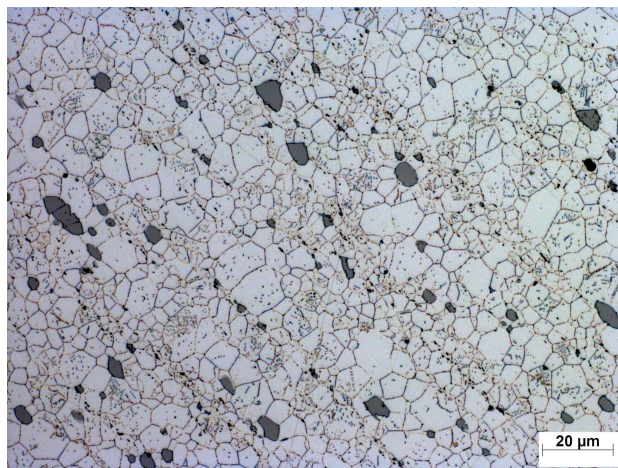


Fig. 1 Microstructure of Elektron 21 alloy, light microscope, etch. 0.5 % nital

Experimental methods

Prior to the electrodeposition of calcium phosphate, the samples were firstly ground with an emery paper of P1000 to ensure similar surface roughness, then rinsed with ethanol, and dried using a stream of hot air. The formation of dicalcium phosphate dehydrate (DCPD) layer was performed by electrodeposition on the sample's surfaces. The chemical composition of electrolyte consisting of reagents 0.1 M $\text{Ca}(\text{NO}_3)_2$, 0.06 M $\text{NH}_4\text{H}_2\text{PO}_4$ and 10 ml.l^{-1} H_2O_2 with a pH of 4.2 using a laboratory apparatus VSP (producer BioLogic SAS France). A three-electrode system consisting of counter electrode (platinum electrode), reference electrode (saturated calomel electrode) and working electrode (sample) was used for electrodeposition process. Electrodeposition was performed with constant potential -1.8 V vs E_{SCE} for 1 hour [10].

The surface morphology of treated samples was assessed in laboratories of the Department of Materials Engineering, FME, University of Žilina, by a microscope Nikon AZ100 with a digital camera using NIS Elements software. Electrodeposition under specified conditions led to the formation of a thin layer of calcium phosphate DCPD (Fig. 2).

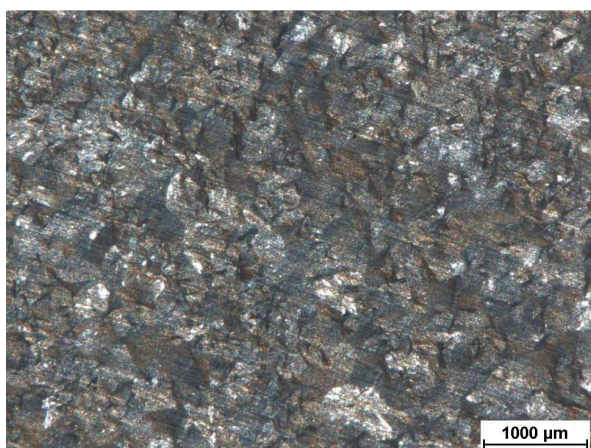
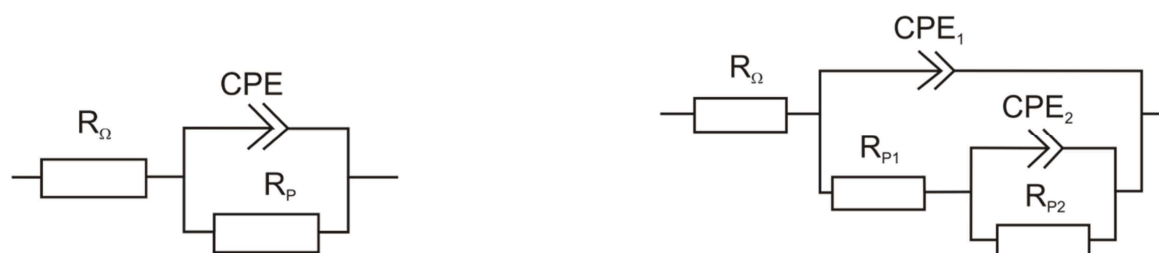


Fig. 2 Morphology of CaP layer on Mg alloy surface

Results and discussion

Corrosion tests were performed by electrochemical impedance spectroscopy (EIS) for the evaluation of corrosion resistance of surface layers after exposure times from 5 minutes to 168 hours in 0.1 M NaCl solution at laboratory temperature simulated sea atmosphere in certain extent. Corrosion electrochemical characteristics were measured and evaluated by potentiostat/galvanostat/frequency response analyser VSP from BioLogic SAS France. A saturated calomel electrode and platinum electrode served as the reference and auxiliary electrodes, respectively. Treated and untreated Elektron21 samples formed the working electrode (a classical three electrode system) in such a way that only 1 cm^2 area of the working electrode surface was exposed to the electrolyte solution in corrosion cell. Measurements were performed at open circuit potential with AC voltage amplitude of 5 mV in frequency range from 100 kHz to 10 mHz. Measured Nyquist plots were analysed by EC-Lab software using equivalent circuits shown in Fig. 3.



a) For Nyquist plots with one capacitive loop

b) For Nyquist plots with two capacitive loops

Fig. 3 Equivalent circuits used for analysis of Nyquist plots

Fig. 3a expresses the equivalent circuit used for Nyquist plots with one capacitive loop and Fig. 3b the equivalent circuit used for Nyquist plots with two capacitive loops. These equivalent circuits use various elements expressing the character of evaluated surface. The equivalent circuit in Fig. 3a represents the situation on the surface of sample when one layer of corrosion product exists. Fig. 3b represents the situation on the material surface when two layers of corrosion products exist (first layer is the double layer and second layer is the layer of corrosion products) or two different areas (first one with good adhesion to the surface and second one as corrosion products at the broken places of the layer with good adhesion to the surface) exist on the surface. In our case, R_Ω is resistance of the solution, R_{p1} and R_{p2} are partial polarization resistances of various mechanisms in corrosion model (e.g. charge transfer, film resistance,...), R_p is mixed polarization resistance or sum of partial polarisation resistances ($R_{p1} + R_{p2}$) and CPE_1 and CPE_2 are constant phase elements of mechanisms corresponding with R_{p1} and R_{p2} , respectively. CPE_1 in second equivalent circuit is constant phase element of the layer of corrosion products [10].

Results from EIS measurements in the form of Nyquist plots are shown in Fig. 4 and Fig. 5 for Elektron 21 samples with ground surface and surface coated by DCPD, respectively.

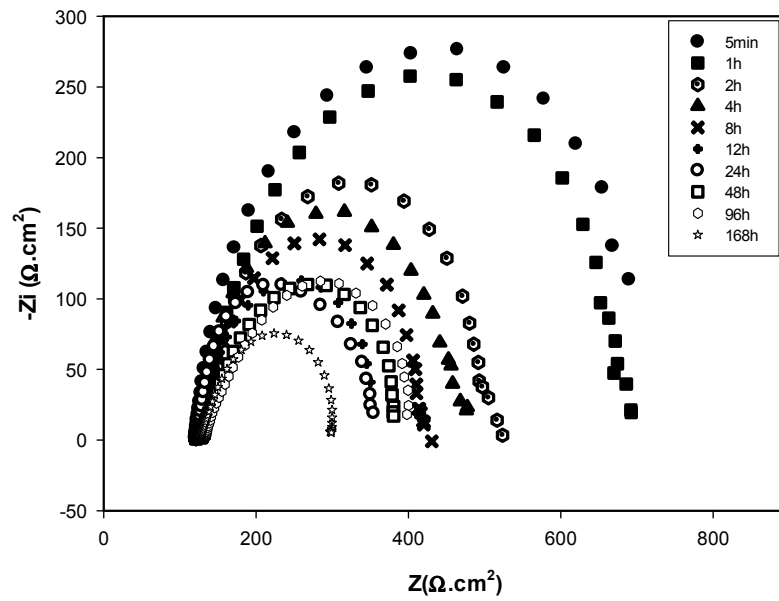


Fig. 4 Nyquist plots of ground Elektron 21 samples after various exposure times

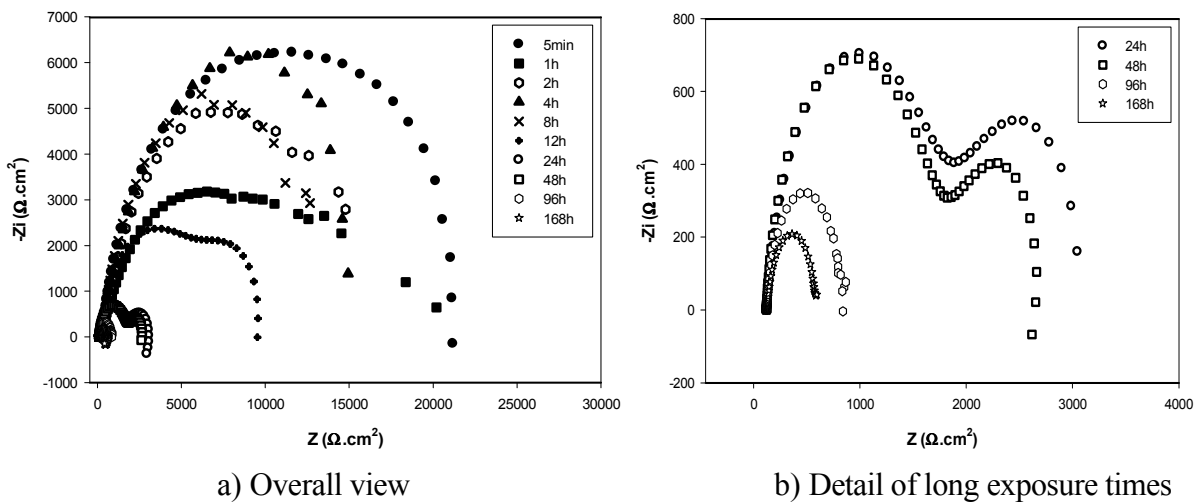


Fig. 5 Nyquist plots of Elektron 21 samples with calcium phosphate coating after various exposure times

A very important characteristic best describing the resistance of the surface layer (or layers) of the certain material against corrosion is a polarization resistance R_p . Based on Nyquist plots analysis the values of polarization resistance R_p were obtained. The values of polarization resistances and other electrochemical characteristics gained after various exposure times on Elektron 21 magnesium alloy samples with out and with DCPD coating are listed in Table 2 and Table 3, respectively.

Table 2 Electrochemical characteristics of ground Elektron 21 samples after selected exposure times

Exp. time	$R_{\Omega} (\Omega.cm^2)$	$CPE_1(\mu F.s^{b_1-1})$	b_1	$R_p (\Omega.cm^2)$
5 min.	119	23.24	0.8603	776
1 h.	121	13.99	0.9331	605
2 h.	122	27.69	0.8855	583
4 h.	123	47.21	0.9045	397
8 h.	123	74.96	0.9414	349
12 h.	129	70.12	0.9552	294
24 h.	123	53.84	0.9363	238
48 h.	124	48.20	0.8942	246
96 h.	130	52.53	0.8476	262
168 h.	129	47.31	0.8969	168

Table 3 Electrochemical characteristics of Elektron 21 samples with DCPD coating after selected exposure times

Exp. time	$R_{\Omega} (\Omega.cm^2)$	$R_{p1} (\Omega.cm^2)$	$R_{p2} (\Omega.cm^2)$	$CPE_1(\mu F.s^{b_1-1})$	$CPE_2(\mu F.s^{b_2-1})$	b_1	b_2	$R_p (\Omega.cm^2)$
5 min.	142	22580	-	23.10	-	0.6871	-	22580
1 h.	145	22873	-	20.46	-	0.6791	-	22873
2 h.	147	18714	-	20.07	-	0.6541	-	18714
4 h.	148	16525	-	20.27	-	0.6981	-	16525
8 h.	146	14550	-	18.88	-	0.6721	-	14550
12 h.	137	7195	2400	21.41	0.000530	0.7357	1	9595
24 h.	125	1724	1220	18.81	0.001220	0.8577	0.8829	2944
48 h.	119	968	1609	16.42	0.000016	0.8391	0.8980	2577
96 h.	122	729	-	42.89	-	0.9063	-	729
168 h.	122	486	-	41.46	-	0.8767	-	486

Potential-controlled electrodeposition process under specified conditions resulted in a thin calcium phosphate dihydrate (DCPD) layer formation (Fig. 2) with the chemical composition $CaHPO_4 \cdot 2H_2O$.

Already after 5 minutes exposure time of ground Elektron 21 samples in corrosive electrolyte representing 0.1 MNaCl solution occurred the formation of oxide (MgO) and hydroxide ($Mg(OH)_2$) corrosion products on the surface layer which is represented by maximum value of polarization resistance ($776 \Omega.cm^2$). After this time there was just the decrease of this characteristic up to its minimum value of $168 \Omega.cm^2$ measured after 168 hours of exposure. This decrease of R_p values was caused by the degradation of the surface layer formed by corrosion products followed by local denudation of the substrate. Moreover, there was an enlarging of the active sample surface participating in the corrosion process. Surfaces of Elektron 21 magnesium alloy samples with DCPD coating showed a substantial increase in polarization resistance values in comparison with ground samples after various exposure times. After 5 minutes of exposure in corrosive solution, the R_p of the samples coated by DCPD ($22580 \Omega.cm^2$) achieved 29-fold higher value compared to that of ground samples after the same exposure time. Maximum value of R_p was reached after 1 hour of exposure ($22873 \Omega.cm^2$). This value was 30 times higher than the maximum R_p value of the samples with ground surface. Corrosion process of Elektron 21 alloy with DCPD coating was

different to that of ground surface. As can be seen from Fig. 2, samples were not covered by DCPD coating uniformly and thus the formation of corrosion products appeared in the places with insufficient coverage after immersion to corrosive environment. This caused increase of the coating compactness, which resulted in an increase of its polarization resistance. However, immediately after immersing the samples to corrosive environment the reaction of DCPD with this environment also occurred, causing its gradual dissolution as reflected by decrease of R_p value ($18714 \Omega \cdot \text{cm}^2$) after two hours of exposure. Local breaks of the coating in which active corrosion process took place can be seen on the samples surface. The development of corrosion process in these local areas led to a gradual degradation of the DCPD surface layer associated with the further decrease of polarization resistance to a minimum value of $486 \Omega \cdot \text{cm}^2$ achieved after 168 hours of exposure in corrosive medium. Despite of losing the comprehensive protection capability of DCPD layer already after 12 hours of exposure, it was noted that the polarization resistance of the surface with DCPD layer was after 168 hours exposure in corrosive environment comparable with the R_p of ground surface after 4 hours exposure. It means that this surface layer provided higher corrosion resistance of the Elektron 21 surface layer at all of the selected exposure times.

Conclusions

On the basis of performed experiments, analysis of the results and their interpretations, we concluded the following conclusions:

- Thin calcium phosphate dehydrate (DCPD) coating prepared by potential-controlled electrodeposition process under specified conditions forms the continuous layer composed of irregularly branched flake-like formations of a different size covering the entire surface.
- The polarization resistance (R_p) value of Elektron 21 samples with DCPD coating ($22580 \Omega \cdot \text{cm}^2$) reached after first 5 minutes of exposure in corrosive medium achieves 29-fold higher value compared to that of ground samples ($776 \Omega \cdot \text{cm}^2$) after the same exposure time. It represents a relevant improvement of surface layer corrosion protection.
- Maximum value of R_p reached on samples with DCPD coating after 1 hour of exposure ($22873 \Omega \cdot \text{cm}^2$) is 30 times higher than the maximum R_p value of the samples with ground surface ($776 \Omega \cdot \text{cm}^2$).
- Prepared DCPD coating provides significant corrosion protection in 0.1 M NaCl solution at $22 \pm 1^\circ \text{C}$ during 12 hours of exposition. Consequently, there is a gradual degradation of the coating and local corrosion processes as evidenced by decrease in polarization resistance values.
- This surface layer provides higher corrosion resistance of the Elektron 21 surface layer compared to ground surface at all selected exposure times.

Acknowledgments

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Literature References

- [1] P. Lyon, I. Syed, T. Wilks, The influence of alloying elements and heat treatment upon properties of Elektron 21 (EV31A) alloy, *Magnesium Technology* (2005) 303-308.
- [2] Sheet MEL-Magnesium Elektron no. 455.
- [3] L.L. Rokhlin, *Magnesium Alloys Containing Rare Earth Metals: Structure and Properties*, Taylor & Francis Eds., (2003).
- [4] L.R. Gill, G.W. Lorimer, P. Lyon, The Effect of Zinc and Gadolinium on the Precipitation Sequence and Quench Sensitivity of Four Mg-Nd-Gd alloys, *Adv. Eng. Mater.*, 9 (2007) 784.

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- [5] G. Song, A. Atrens, Understanding Magnesium Corrosion—A Framework for Improved Alloy Performance. *Advanced Engineering Materials*, Vol. 5, No. 12 (2003) 837–858.
- [6] X. Zhang, Q. Li, L. Li, P. Zhang, Z. Wang, F. Chen, Fabrication of hydroxyapatite/stearic acid composite coating and corrosion behavior of coated magnesium alloy. *Mater. Letters*. (2012) 76–78.
- [7] F. Nový, et al., Very high cycle fatigue behaviour of as-extruded AZ31, AZ80, and ZK60 magnesium alloys. In *International journal of materials research. Zeitschrift für metallkunde.*, Vol. 100, No. 3, (2009) 288–291.
- [8] M. Kasenčák, P. Palček, A. Námešný, Internal damping of magnesium alloy in dependence on amplitude deformation, *Mater Eng.* 15, (2008) 101–104.
- [9] G. Lorimer, P. Apps, H. Karimzadeh, J. King, Improving the performance of Mg-Rare Earth alloys by the use of Gd or Dy additions, *Materials Science Forum* 419–422 (2003) 279–284.
- [10] F. Pastorek, B. Hadzima, Study of calcium phosphate (DCPD) electrodeposition process on a Mg–3Al–1Zn magnesium alloy surface. *Mater Eng.* 19, (2012) 54–63.

V. Material Properties

Influence of temperature on the electrochemical characteristics of Ti-6Al-4V

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Keywords: Titanium, Ti-6Al-4V, ground surface, polished surface, corrosion resistance, electrochemical measurements, potentiodynamic tests

Abstract. Titanium is not only the most widely used biomaterial for medical implants, but with its very good mechanical properties, corrosion resistance and low density is also applied in many sectors of industry (aerospace, military, aviation, machinery, energetics, chemicals, etc.). In this paper it is described the influence of temperature on the electrochemical characteristics of Ti-6Al-4V alloy. The surface was mechanically ground and polished by chemical-mechanical process. Basic electrochemical characteristics were determined by potentiodynamic tests in 0.1M NaCl solution at different temperatures. The obtained results were analysed by the Tafel-extrapolation method. Finally, a modified Arrhenius relation was used for determination of activation energy. The activation energy of ground and chemical-mechanical polished surface is nearly three times higher than activation energy of only ground surface.

Introduction

Titanium and its alloys have been frequently used for many engineering components due to its beneficial properties, such as low density, low modulus elasticity, excellent corrosion resistance and biocompatibility. Titanium and its alloys are preferred materials for hard tissue replacements because of their excellent mechanical properties, corrosion resistance and biocompatibility [1-3].

Generally, many of these alloys have endless possibility of application. More of the light non-ferrous materials have considerable attention in automotive, aerospace and ship industries application to increase the fuel efficiency and to reduce the environmental pollution. Some of titanium alloys are used in the field of energy, like supporting structures of wind turbines or in devices that operate in the long-term contact with seawater. In engine applications, titanium is used for rotors, compressor blades, hydraulic system components and nacelles. For the chemical industry titanium material is an increasingly popular for production or simple stuffing chemical reactors operating in extreme conditions and requiring high corrosion resistance [4,5].

In fact, titanium oxides have found some areas of applications like converting solar energy, photocatalytic syntheses, photocatalytic degradation of certain organic pollutants and the electrolytic production of chlorine. The titanium 6Al-4V alloy represents for almost 50% of all alloys used in aircraft applications [6]. Ti-6Al-4V alloy is one of the most widespread and the most development heterogeneous alloy of the $\alpha + \beta$ type. Aluminum is stabilizer of the close-packed hexagonal alpha phase. On the other hand, vanadium is beta stabilizer of this body-centered cubic phase. Alloys of this kind of crystal structures have excellent mechanical properties, which can be increased by heat treatment. On the whole, $\alpha + \beta$ titanium alloys are not only heat treatable and weldable, but the strength levels are medium to high and they can be superplastically formed. On the other side, high

temperature creep strength is not as good as alpha alloys and cold forming may be limited, but hot forming qualities are normally good [7,8].

The aim of this paper is to review the influence of temperature between 10°C and 80°C on the electrochemical characteristics of Ti-6Al-4V alloy. Based on the requirements of industry, the main task was to compare two surfaces - grinded surface and polished surface, which were obtained by special process.

Experimental method

Ti-6Al-4V alloy with chemical composition listed in Table 1 was used in this study. The material was heat-treated at 768-772°C for 45 minutes. Microstructure of the investigated alpha beta experimental material (Fig. 1) was made by ZEISS AXIO OBSERVER Z1 light microscope using the program Axion Vision rel. 4.8. Two-phased microstructure is formed by close-packed hexagonal α -phase (light grains) and body-centered cubic β -phase (dark grains) [8]. Proportion of alpha phase is around 60%.

Table 1. Chemical composition of Ti-6Al-4V

Component	Al	V	Fe	C	N	H	O	Y	O+N
Wt.%	6.38	4.21	0.19	0.011	0.001	<0.002	0.15	<0.001	0.159

Electrochemical characteristics are based on the electrochemical corrosion in conductive environments. They are used for establishing the electrochemical corrosion characteristics of materials in different corrosion conditions, for the basic examination of the mechanism of corrosion of materials as well as for controlling of the conditions in practice. Based on the results of electrochemical methods can be calculated the estimated corrosion rate of the material in the required environment, assume the sensitivity to different kind of corrosion, also corrosion cracking, etc. [9].

Electrochemical characteristics of Ti-6Al-4V alloy were evaluated by electrochemical tests in 0.1M NaCl solution at 10 ± 0.5 , 20 ± 0.5 , 30 ± 0.5 , 40 ± 0.5 , 50 ± 0.5 , 60 ± 0.5 , 70 ± 0.5 and 80 ± 0.5 °C. The temperature in the corrosion cell was regulated by thermostat that operated on required temperatures. The electrochemical tests were carried out using a classical three electrodes cell with platinum as counter electrode, saturated calomel electrode SCE (+0.242V vs. SHE) as reference electrode and the sample as working electrode. Potentiodynamic polarization measurements were performed on ground and polished samples using a modular 5 channels potentiostat VSP produced

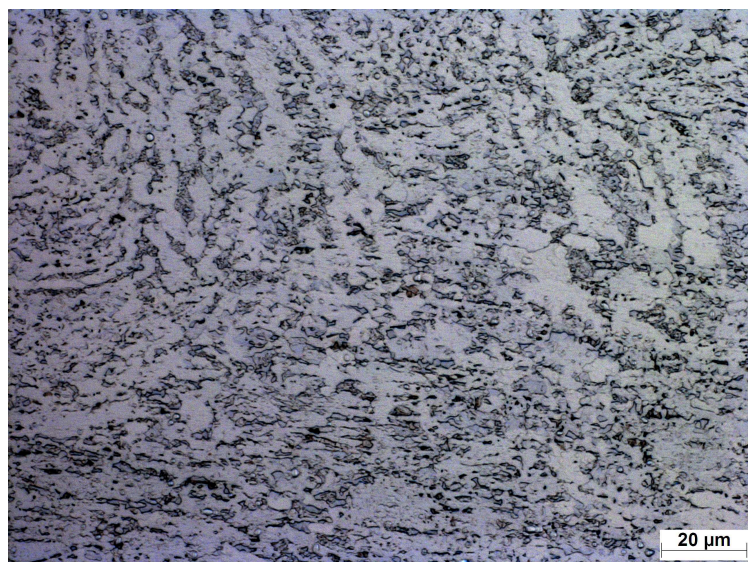


Fig. 1 Microstructure of Ti-6Al-4V, etched by 15ml HF, 30ml HNO₃ and 50ml H₂O

by BioLogic SAS France. The potentiodynamic curves were obtained at various temperatures in the potential range between -250 and +1200mV versus free potential after 5 minutes of initial immersion with constant voltage scan rate of 1mV.s^{-1} . Measured sample area was 1 cm^2 . Schematic diagram of experimental setup is described elsewhere [10]. Based on the Tafel analysis performed by EC-Lab program V10.12, the following values were determined - corrosion potential E_{corr} , corrosion current density I_{corr} , Tafel coefficients b_c , b_a and also the values of instantaneous corrosion rate v_{corr} .

The ground surface was achieved with plane silicon carbide paper 180 grit emery for 3 minutes, then 500 grit emery for 2 minutes. For polished surface was subsequently used MD-Largo roll with DiaPro Allegro/Largo suspension for 10 minutes. The final third step for chemical-mechanical polishing was obtained by OP roll with a mixture of colloidal silica (OP-S) and hydrogen peroxide (30%) for 10 minutes, too.

Results and discussion

The obtained potentiodynamic polarization curves for ground surface plotted in semi-logarithmic scale in 0.1M NaCl solution are shown on Fig. 2a, the potentiodynamic curves for polished surface are shown on Fig. 2b. The measurements were repeated three times for each condition. Table 2 listed the thermodynamic and kinetic characteristics for grinded surface for each temperature together with Tafel constants obtained from the polarization curves. The Tafel parameters of polished surface are summarized in Table 3.

Table 2 Tafel analysis results for the ground surface of Ti-6Al-4V in 0.1M NaCl solution

Temperature	Electrochemical characteristics				
	$E_{corr} \text{ vs } E_{ref}$ [mV]	i_{corr} [$\mu\text{A.cm}^{-2}$]	b_c [mV]	b_a [mV]	r_{corr} [mm.year ⁻¹]
10°C	-510	0.4	89	84	0.01
20°C	-503	0.3	85	90	0.01
30°C	-543	0.5	78	88	0.02
40°C	-392	0.5	81	86	0.02
50°C	-465	0.6	85	85	0.02
60°C	-399	0.8	78	89	0.03
70°C	-395	0.6	73	81	0.02
80°C	-429	0.8	76	91	0.03

Table 3 Tafel analysis results for the polished surface of Ti-6Al-4V in 0.1M NaCl solution

Temperature	Electrochemical characteristics				
	$E_{corr} \text{ vs } E_{ref}$ [mV]	i_{corr} [$\mu\text{A.cm}^{-2}$]	b_c [mV]	b_a [mV]	r_{corr} [mm.year ⁻¹]
10°C	-495	0.1	87	76	0.004
20°C	-373	0.1	88	79	0.004
30°C	-434	0.2	82	72	0.008
40°C	-417	0.2	93	80	0.008
50°C	-430	0.3	86	72	0.009
60°C	-440	0.6	90	99	0.022
70°C	-303	0.4	94	77	0.013
80°C	-280	0.5	129	91	0.016

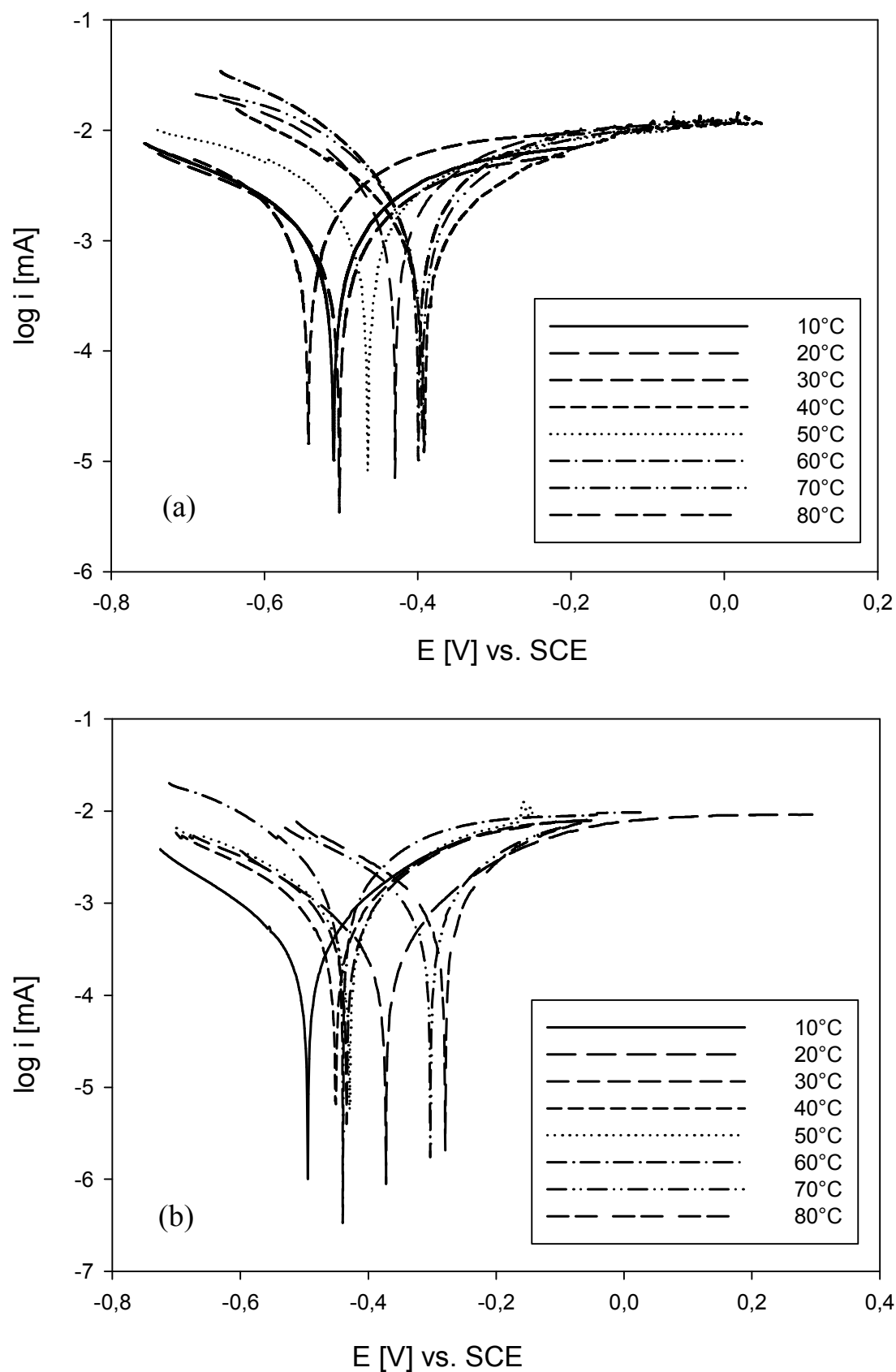


Fig. 2 Potentiodynamic polarization curves of Ti-6Al-4V for ground (a) and polished (b) surface measured between 10°C and 80°C.

The polished samples measured from 10 to 80°C showed more positive E_{corr} value (from -495 to -280mV), compared with grinded samples, which showed an E_{corr} value from -510 to -392mV

(Tables 2, 3). This result revealed that the chemical-mechanical polished surface is electrochemically nobler and hence thermodynamically more stable for each temperature.

In terms of kinetics, the values of corrosion current densities for both surfaces were different. The values of chemical-mechanical polished surface were from 0.1 to 0.6 $\mu\text{A}.\text{cm}^{-2}$, while the values of ground surface were from 0.3 to 0.8 $\mu\text{A}.\text{cm}^{-2}$ (Tables 2, 3). These results demonstrated that the chemical-mechanical polished surfaces have a considerable effect on i_{corr} . These results are important in comparing the corrosion rate, too. As seen in Table 2 and Table 3, the corrosion rate of ground surface is really higher (from 0.01 to 0.03 $\text{mm}.\text{year}^{-1}$) than corrosion rate of polished surface (from 0.004 to 0.016 $\text{mm}.\text{year}^{-1}$).

The influence of the temperature for the rate of corrosion is based on Arrhenius relation

$$k = A.\exp(-E_a/RT) \quad (1)$$

where k is rate constant, A is pre-exponential factor, E_a is activation energy, R is the universal gas constant and T is the absolute temperature in Kelvin. Based on this relation, i_{corr} is the function of temperature [11]

$$i_{\text{corr}} = f(T) = A.\exp(-E_a/RT) \quad (2)$$

The activation energy for these corrosion processes showed the Fig. 3, where are the curves of $\ln i_{\text{corr}}$ versus $1/T$ and characterized the sensitivity of ground and polished surfaces. The activation energy of ground surface was 7.98 $\text{kJ}.\text{mol}^{-1}$ and the activation energy of chemical-mechanical polished surface was 21.87 $\text{kJ}.\text{mol}^{-1}$. These results confirmed that the polished surface led to decrease of its corrosion activity.

Table 4 Activation energy of grinded and polished surface of Ti-6Al-4V alloy

Surface of alloy	E_a [$\text{kJ}.\text{mol}^{-1}$]
ground	7.98
polished	21.87

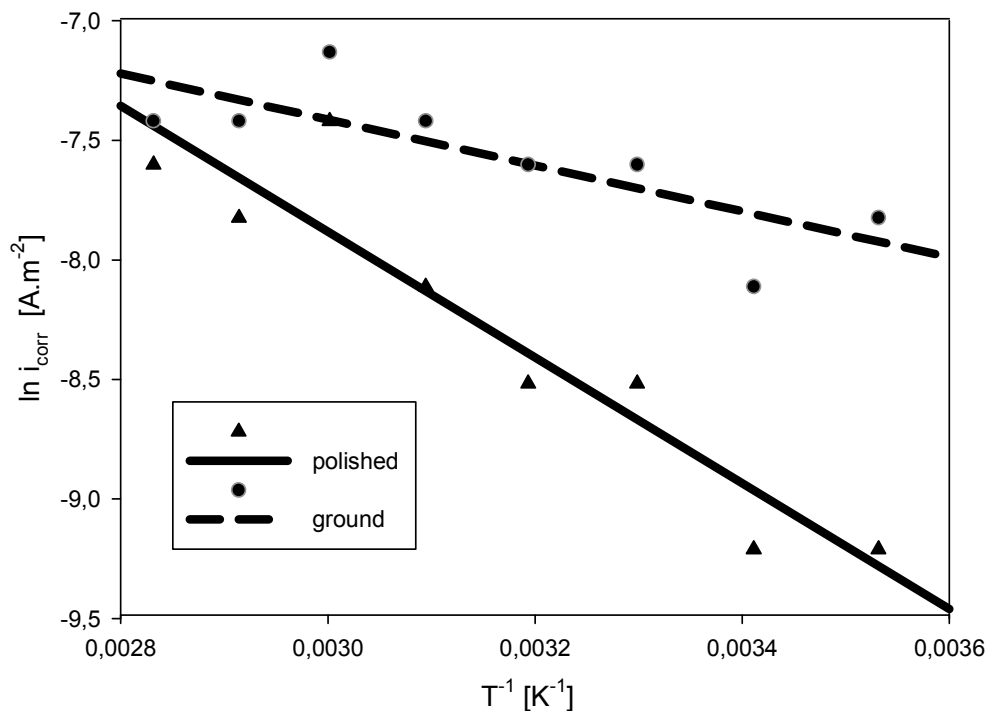


Fig. 3 $\ln i_{\text{corr}}$ versus $1/T$ plots for Ti-6Al-4V in 0.1M NaCl solution

Conclusions

Based on the requirements of industry the electrochemical characteristics of Ti-6Al-4V alloys were measured. It was necessary to obtain the potentiodynamic polarization curves of ground and polished surfaces at various temperatures between 10°C and 80°C used a step of 10°C. The results of the Tafel extrapolation showed significantly lower corrosion current density and corrosion rate of chemical-mechanical polished surfaces of these titanium alloys compared to the grinded samples at all conditions.

According to the Arrhenius equation, the activation energy of both surface conditions was calculated. Actually, the improvement of corrosion resistance of chemical-mechanical polishing surface of titanium alloy was proved by higher value of the activation energy (21.87 kJ.mol⁻¹). The value of activation energy for grinded samples was approximately three times lower (7.98 kJ.mol⁻¹).

Acknowledgment:

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References

- [1] W.M. Thomas, E.D. Nicholas, Friction stir welding for the transportation industries. *Mater Des.* 18 (1997) 269-73.
- [2] M.A. Sutton, B. Yang, A.P. Reynolds, R. Taylor, Microstructural studies of friction stir welds in 2024-T3 aluminum. *Sci Eng.* 323 (2002) 160-6.
- [3] Y.T. Sul, C.B. Johansson, Y. Jeong, T. Albrektsson, The electrochemical oxide growth behaviour on titanium in acid and alkaline electrolytes. *Med Eng Phys* 23 (5) (2001) 329-46.
- [4] I.J. Polmear, *Light alloys: metallurgy of the light metals*, third ed., Arnold, London, 1995.
- [5] W.F. Smith, *Structure and properties of engineering alloys*, second ed., McGraw-Hill, 1993.
- [6] M. Gratzel, Photoelectrochemical Cells. *Nature* 414 (2001) 338-344.
- [7] P. Skočovský, P. Palček, R. Konečná, L. Várkony, *Construction materials*, University of Žilina, Žilina. 2000, (in Slovak).
- [8] L. Škublová, B. Hadzima, L. Borbás, M. Vitosová, The influence of temperature on corrosion properties of titanium and stainless steel biomaterials, *Mater Eng – Mater Inž* 15 (4) (2008) 18-22.
- [9] B. Hadzima, T. Liptáková, *Fundamentals of electrochemical corrosion of metals*, University of Žilina, Žilina. 2008, (in Slovak).
- [10] J. Vrátná, B. Hadzima, M. Bukovina, M. Janeček, Room temperature corrosion properties of AZ31 magnesium alloy processed by extrusion and equal channel angular pressing, *J Mater Sci* 48 (2013) 4510-16.
- [11] B. Hadzima, M. Mhaede, F. Pastorek, Electrochemical characteristics of calcium-phosphatized AZ31 magnesium alloy in 0.9 % NaCl solution, *J Mater Sci: Mater Med* 25 (5) (2014) 1227-37.

The corrosion properties of EN AW 7075 aluminium alloy in power industry

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Keywords: aluminium alloy, aircraft industry, corrosion resistance, fatigue properties

Abstract:

The study in this paper aimed on the corrosion properties of aluminium alloys used in the power industry. The corrosion characteristics were evaluated in the initial state and state after severe plastic deformation of aluminium alloy AlZnMgCu. Due to the frequent interaction of fatigue failure accompanied corrosive failure (e.g. aircraft wings, turbine blades etc.) fatigue characteristics of selected alloy were evaluated. Standard corrosion characteristics such as corrosion potential, polarization resistance, corrosion rate and the corrosion products were evaluated for both states of an alloy in distilled water and SARS during exposition reaching 6 months.

Introduction:

The aluminium alloys and their composites are potential materials for light weight structures, specifically for the aircraft industry. Around 60% of the total consumption of aluminium alloys in the aircraft industry served for turbine blades, aircraft engines, compressors and coatings for low- and high-pressure turbine engines. These alloys must meet the high fracture toughness, high formability, high strength and hardness, excellent conductivity which makes them important in the energy sector [1-4]. Another requirement is a high fatigue resistance, resulting in a higher fatigue life of aircraft parts made of aluminium alloys. At a lower resistance to fatigue, failure could arise from an interaction of fatigue loading with corrosion degradation. Alloy EN AW 7075 has a relatively high resistance to corrosion, which can be enhanced by suitably chosen surface finish, respectively technology of anodizing [5-6].

Due to the high demands of today's aircraft industry's this contribution is focused on the corrosion and fatigue properties of aluminium alloy EN AW 7075 in aqueous solutions consisting of distilled water as reference electrolyte and SARS as simulated acid rain solution.

Experimental material and methods:

An aluminium alloy EN AW 7075 (AlZn5.5MgCu) in two states with the chemical composition: 89.4 % Al, 0.19 % Cr, 1.80 % Cu, 0.14 % Fe, 2.49 % Mg, 0.02 % Mn, 0.06 % Si, 5.74 % Zn was used as experimental material. The aluminium alloy in its initial state was heat-treated as follows: solution annealing, cold forming and natural aging. Subsequently, before the application of severe plastic deformation of the alloy subjected to solution annealing 470 °C / 6 h with quenching at room temperature. Intense plastic deformation was carried out by process ECAP at room temperature with 1 pass through the ECAP die. It was subsequently realized artificial aging at 120 °C/24 h. Metallographic analysis in the initial state and in the state after ECAP was performed by standard metallographic procedure. The sample surfaces were documented by light microscopy Olympus Vanox-T. EDX analysis of particles and corrosion products was realised by scanning electron microscope JEOL JSM-7000F and analyzer INCAx-sight. The corrosion potential of the aluminium alloy were measured against a saturated calomel electrode SCE in a solution of distilled water and SARS (0.01 mM HNO₃; 1 mM NaCl; 1 mM (NH₄)₂SO₄). The polarisation curves were measured

and corrosion potential, corrosion current density were evaluated by Tafel method and polarization resistance according to Stern method. Corrosion characteristics were monitored during 6 months exposure in these environments. The fatigue properties on samples were evaluated using the torsional load in initial state and state after ECAP at a frequency of 35 Hz.

Results and discussion

Microstructure and analysis of particles of the aluminium alloy in the initial state and the state after ECAP are documented in Fig. 1 and Fig. 2. Fig. 2 show microstructure after ECAP with presence of visible deformation bands, which occurred after one pass through the ECAP die. These deformation bands pointed out uneven deformation along cross section the samples. According to EDX analysis are particles in both state based on AlFeCu, AlMgCuFeZn and AlMgCuZn.

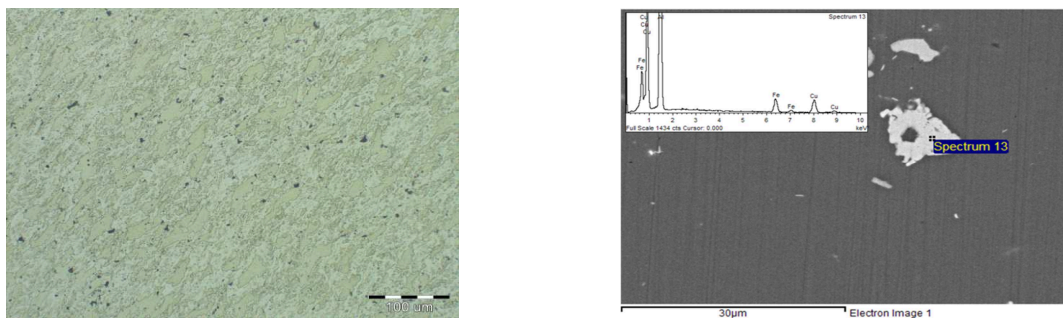


Fig. 1 Microstructure and EDX analysis of the aluminium alloy in initial state

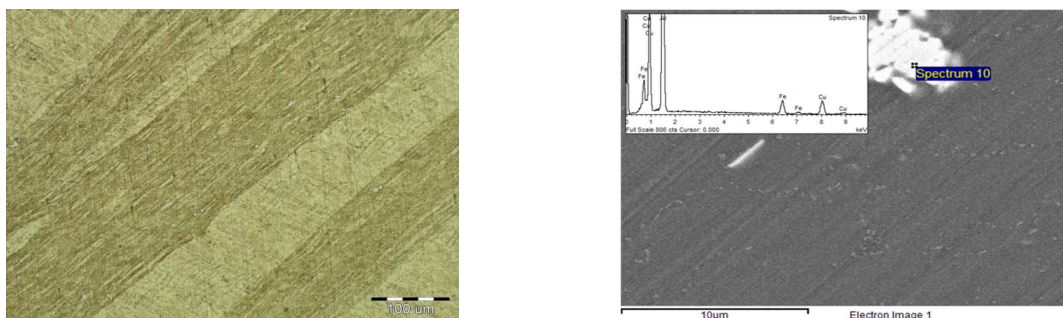


Fig. 2 Microstructure and EDX analysis of the aluminium alloy after ECAP and heat treatment

The open circuit potentials measured in these environments are shown in Table 1 and are graphically illustrated in Fig. 3. From the dependence of the open circuit potential with time, it can be stated that the open circuit potential getting less negative values with increasing exposure time and aluminium alloy became passivated in distilled water. The highest protective efficacy was achieved in distilled water in both states to produce a solid protective layer on the surface of the alloy. An open circuit potential for aluminium 7075 in SARS environment is stable for whole exposure and there was no significant change in values of potential during exposure time and from the corrosion point of view surface was active. The surface of the samples is showed on Fig. 4.

Table 1 Open circuit potential of aluminum alloy in both state / * distilled water ** SARS

Material	E _{SCE} [mV] in initial state								
	1 [min]	10 [min]	30 [min]	60 [min]	1200 [min]	1440 [min]	14400 [min]	175680 [min]	263520 [min]
EN AW 7075 *	- 736	- 501	- 410	- 387	-360	- 325	- 491	- 216	- 80
EN AW 7075 **	- 607	- 600	- 578	- 552	- 562	- 549	- 554	- 559	- 566

Material	E_{SCE} [mV] after ECAP								
	1 [min]	10 [min]	30 [min]	60 [min]	1200 [min]	1440 [min]	14400 [min]	175680 [min]	263520 [min]
EN AW 7075 *	-615	-554	-500	-477	-306	-460	-178	-20	-54
EN AW 7075 **	-795	-803	-758	-694	-535	-546	-570	-376	-604

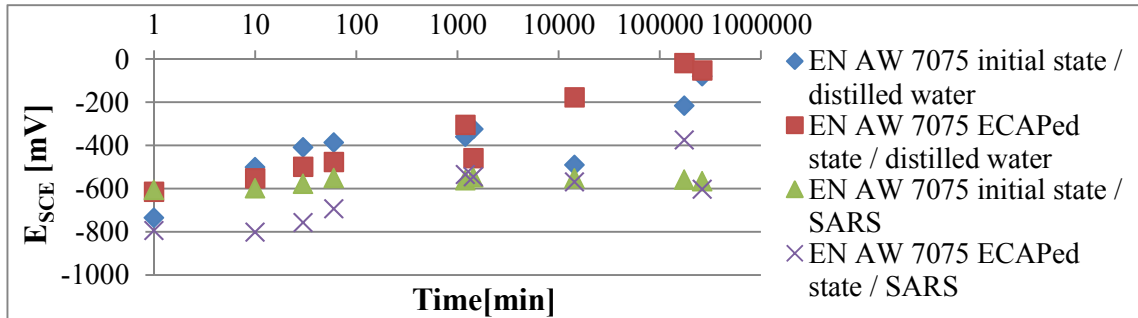


Fig. 3 Dependence of corrosion potential E_{SCE} on the exposure time of samples in distilled water and in SARS

The surface after 6 months of the exposure in distilled water in case of samples A (initial state) and C (after ECAP) were covered with thin layer of corrosion products. In the case of surfaces exposed to distilled water, the products consist mainly of K, Ca, Cu, Zn and very low concentration of Cl. After exposure in SARS for samples B (initial state) and D (after ECAP) surfaces were covered with a thick layer of corrosion products with good adhesion. Conversely surfaces exposed to SARS in terms of solution elements are based on Fe, Cu, Zn, S, Cl.

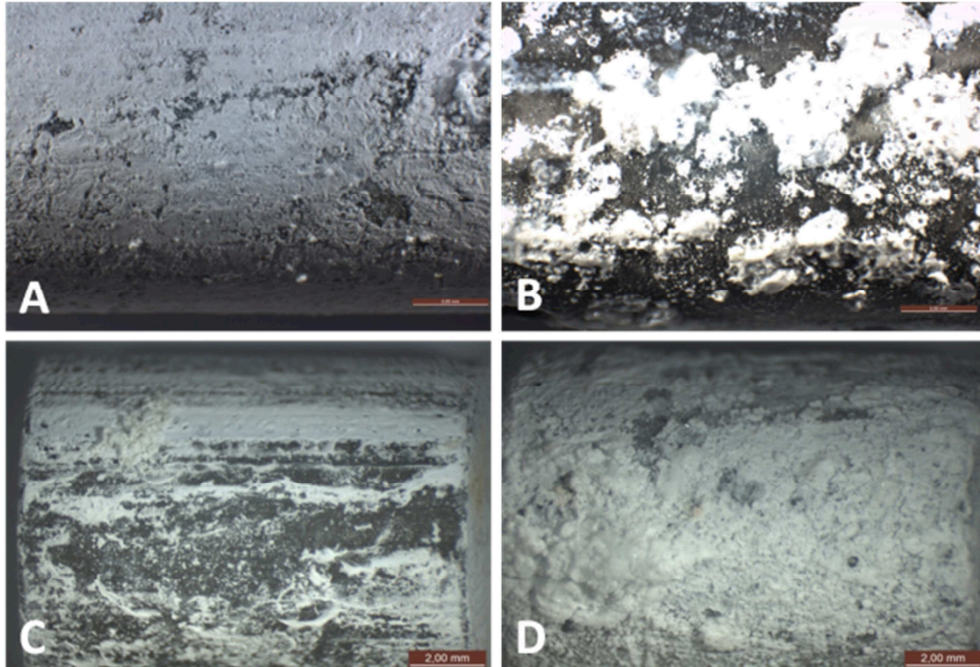


Fig. 4 The surface of samples in initial state / distilled water, after exposure 6 months

On Table 2 are measured results $E = (i=0)$, i_{corr} according Tafel and R_p according to Stern method. It is clear from both Tafel and Stern methods that ECAP procedure activated surface of aluminium alloy 7075 and corrosion reaches app. 50 times higher values of corrosion rate in SARS than in distilled water and ECAP treated sample show 8 times higher values than initial state in the same solutions - SARS.

Table 2 The measured results obtained by Tafel and Stern methods

State		0 [min]		263 520 [min]	
		distilled water	SARS	distilled water	SARS
Initial	$E(i=0)$ [mV]	- 532	- 629	- 511	- 512
	i_{corr} [$\mu\text{A}/\text{cm}^2$]	0.50	0.74	0.96	0.79
	R_p [$\text{k}\Omega\cdot\text{cm}^2$]	76	26	210	79
ECAP	$E(i=0)$ [mV]	- 555	- 636	- 417	- 478
	i_{corr} [$\mu\text{A}/\text{cm}^2$]	0.58	1.15	0.13	6.24
	R_p [$\text{k}\Omega\cdot\text{cm}^2$]	69	38	662	18

The partial results of the oblique branches Wöhler curve is illustrated on Fig. 5. From the partial results of the oblique branches Wöhler curve, we can conclude that higher resistance to fatigue failure of the alloy is in state after ECAP. At a tension of approx. 300 MPa alloy withstand about 4 000 cycles more. At lower tension approx. 170 MPa alloy withstand about 58 000 cycles more than in the initial state. The crack propagates from free surface to the inner space of the specimen where violation occurs in a direction perpendicular to the axis of the sample.

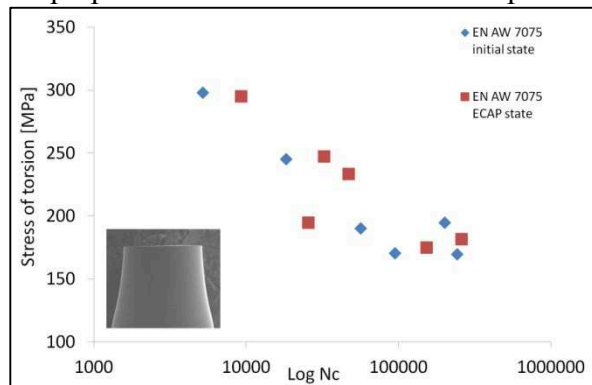


Fig. 5 Diagonal branch of the Wöhler curve of EN AW 7075

Conclusion:

On the basis of the experimental program, we can state the following conclusions:

- The microstructure after severe plastic deformation showed characteristic deformation bands.
- The open circuit potentials for both states of the aluminium alloy 7075 obtained more positive values of potential (less negative values) after 6 months exposure in distilled water. On the other hand, the open circuit potentials in SARS solution, active state, R_p values were lower in distilled water. The layer of corrosion products on the surface of the samples in a distilled water was thinner than in SARS.
- It is remove from both Tafel and Stern methods show that ECAP procedure activated surface of aluminium alloy 7075 and corrosion reaches app. 50 times higher values of corrosion rate in SARS than in distilled water. ECAP treated sample shows 8 times higher values than initial state at the same solutions - SARS.
- Based on the partial results of fatigue tests, we can assume a higher fatigue life of the alloy in the state after severe plastic deformation. Failures of the samples were the same in both cases, it means fatigue failure took place in a direction perpendicular to the axis of the samples.

References:

- [1] Nakai, M., Eto, T.: New aspects of development of high strength aluminum alloys for aerospace applications. In Materials Science and Engineering A285, 2000, pp. 62-68
- [2] Heinz, A. et al.: Recent development in aluminium alloys for aerospace applications. In Materials Science and Engineering A280, 2000, pp. 102-107
- [3] Vogelesang, L.B. et al.: Development of fibre metal laminates for advanced aerospace structures. In Journal of Materials Processing Technology 103, 2000, pp 1-5

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- [4] Zhang, Y.K. et al.: Effect of laser shock processing on the mechanical properties and fatigue lives of the turbojet engine blades manufactured by LY2 aluminum alloy. In *Materials and Design*, 30, 2009, p. 1697-1703
 - [5] Rajendran, R. et al.: Condition assessment of gas turbine blades and coatings. In *Engineering Failure Analysis*, 18, 2011, pp. 2104–2110
 - [6] Puretas, I. et al.: Design and mechanical property analysis of AA1050 turbine blades manufactured by equal channel angular extrusion and isothermal forging. In *Materials and Design*, 52, 2013, pp. 774-784

VI. Safety Issue

BLEVE - CASES, CAUSES, CONSEQUENCES, AND PREVENTION

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Keywords: BLEVE; Boiling liquid expanding vapor explosion; NH₃

Abstract

Corrosion is typical of the damage that occurs in ageing pressure vessels and pipelines used in industrial processes as a result of reactive products inside or aggressive environmental conditions on the outside. Motivation for this article is to summarize cases, causes, consequences and prevention in terms of prediction models for the explosion pressure from BLEVEs. The contribution deals with real scenarios of accidents associated with transport and storage pressurized facilities with corrosive flammable chemicals. While the LPG, propane and butane BLEVEs are well described in the literature, the information about corrosive and toxic flammable substances are rather scarce. The study presents the results of hazardous zone calculation for the event of ammonia corrosive non-flammable chemical releases. For calculations of the BLEVE overpressure, AICHE's Prugh's and Baker's models together with Effects 9.0.8. Rupture of vessels model were used for this study.

Introduction

BLEVE is an explosion resulting from the failure of a vessel containing a liquid at a temperature significantly above its boiling point at normal atmospheric pressure. The vessel rupture can be due to an excessive pressure or weakening of the vessel walls due to the active corrosion process. Corrosion is typical of the damage that occurs in ageing pressure vessels and pipelines used in industrial processes as a result of reactive products inside or aggressive environmental conditions on the outside. Corrosion is considered to lead at BLEVE which is a fairly well-known and well documented explosion phenomenon. A misconception is surprisingly prevalent that BLEVE occurs only with flammable chemicals. The fact is that one-fifth of all BLEVEs occur with non-flammable pressurized liquefied gases. Unfortunately no comprehensive database of all, or even most, of the BLEVEs that have occurred exists. From the 88 of notable BLEVE incidents compiled by [1], it is possible to evaluate the approximate frequency of causative events, from which 2% belongs to mechanical failure caused by corrosion. This assessment is limiting to a sample size of 100 m³ and comprises only of some of the major accident that have occurred across the world from 1926 onwards. Abbasi et al., 2007 [1] illustrates the variety of toxic chemicals under which BLEVEs have occurred in the last 90 years and the destruction that BLEVEs cause in terms of death and injured people. Among major BLEVEs with toxic dispersion, ammonia involved 10%. The scope of this contribution is to compare three existing models - Prugh's [2] and Baker's [3] and TNO's Rupture of vessels [1] for predicting the overpressure of a vessel burst.

Previous studies

Little research has been carried out on bursting vessels. The number of methods for calculating the effects is therefore limited. Most of the research deals with pressure vessels with ideal gases. Just a few studies have been devoted to vessels filled with non-ideal gases and liquids and very little studies have been devoted to non-flammable liquids. The most recent study has been published by Bubicco et al. [4]. This study have demonstrated that the two most used simplified methods for estimating the trend of overpressure vs. distance in case of gas explosions give rise to rather different profiles in the near field, which become closer in the far field, where the absolute values are lower. We adopted the thermodynamic method of Baker et al., [3] and Prugh et al., [2] according to [1] in conjunction with the SVEE estimate of explosion energy. According to the Fig. 1, the results of the adapted models agree well with the results of [4].

Table 1 Distance (m) comparison of the TNO's with developed Baker's and Prugh's.

Initial pressure [bar abs]	Vessel's volume [m ³]							
	10				1000			
	Baker		Prugh		Baker		Prugh	
11.40	16.00 ^a	15.00	11.50 ^a	10.00	80.50 ^a	80.00	45.00 ^a	46.00
9.84	15.00 ^a	13.00	10.40 ^a	9.00	76.20 ^a	77.00	42.00 ^a	43.00
8.42	14.00 ^a	12.00	9.70 ^a	9.00	72.00 ^a	72.70	39.00 ^a	40.00
6.00	11.75 ^a	10.75	8.25 ^a	7.00	61.00 ^a	63.70	32.50 ^a	34.00
4.30	9.25 ^a	9.35	5.80 ^a	6.00	49.50 ^a	55.40	28.00 ^a	29.00

^a value calculated by [4]

Using the Baker's method far and close range are treated differently; the energy of explosion is calculated by means of the Brode's equation. When the explosion occurs at ground level, the calculated value of the energy is conventionally multiplied by 2 to take into consideration ground effects, like the reflection of the shock wave, even if this is just an approximation, which does not properly represent the complexity of a real explosion. The procedure by Prugh's has some similarities with that of Baker described in the previous paragraph. Also in this case the maximum overpressure of the shock wave, i.e. the one at the contact surface between the expanding gas sphere and the air, has to be evaluated. In Prugh's method, differently from Baker's one, the explosion energy is calculated assuming an isothermal expansion of the ideal gas, which also is not a correct hypothesis in the case of ammonia under exam.

Results and discussions

The TNO's rupture of vessel model is described for several different types of vessel ruptures leading to blast and fragmentation [1]. This model is more adequate than Prugh's or Baker's models. It is yet able to render more accurate predictions. This derives from the complexity of the physical phenomenon, the high number of parameters involved, the variability of the real geometrical configuration and of the physical conditions before the explosion, and so on. In order to check the differences in the estimates obtained applying the two methods, a number of accidental scenarios have been simulated and the overpressure profiles as a function of the distance from the centre of the explosion have been reported and compared. The examined scenarios differ in terms of substance involved, total gas volume, operating conditions and geometrical configuration: in particular, a cylindrical and a spherical vessel have been considered, with volumes of 10 m³, 100 m³ (cylindrical) and 1000 m³ (spherical), respectively. Fig. 1 shows the overpressure profiles as a function of the distance from the 10 m³ tank center, for the two models at different values of the burst pressure: since both models assume circular symmetry, the profiles are identical for any directions.

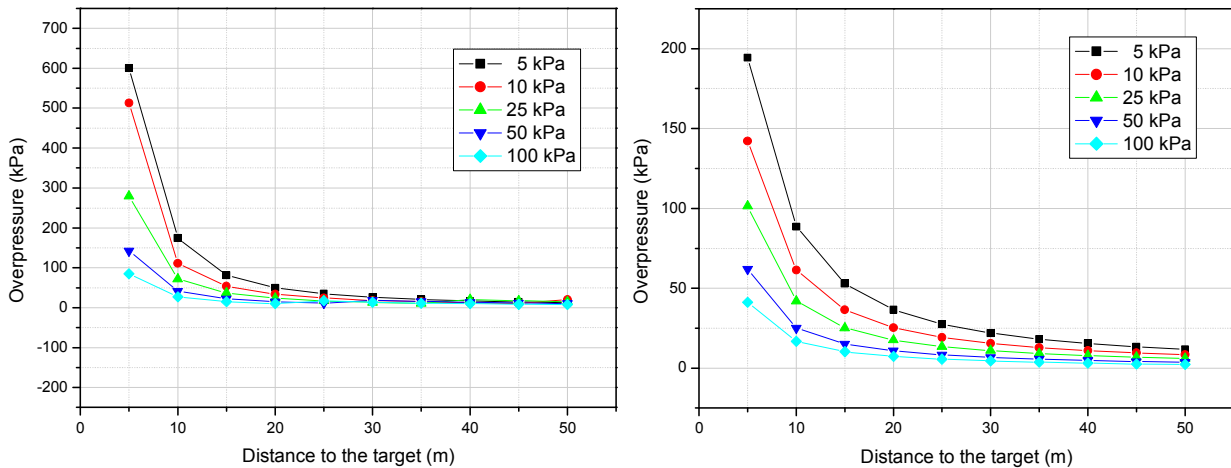


Figure 1 Comparison of the a) Baker's (left) and b) Prugh's (right) models with TNO for a 10 m³ cylindrical ammonia vessel.

It can be observed from Fig. 1a, b that for a given model, the local overpressure varies remarkably with the burst pressure for relatively small distances from the center of the explosion, while at larger distances a much lower difference in the overpressure is experienced, so that the influence of the burst pressure is much more important in the proximity of the exploding vessel, rather than at larger distances. At any given initial tank pressure, if the results of the two models at a given distance are compared, it can be noticed that TNO's model always provides larger values of the overpressure, turning. The value of 30 kPa is usually assumed as the overpressure threshold giving rise to immediately lethal effects on humans, and to domino effects for structures. Therefore, the intersections of the pressure profiles with the horizontal line at 30 kPa will give an approximate safety distance, beyond which significant physical injuries and/or destructive damages to structures are not expected.

Table 2: Distance (m) to 30 kPa for ammonia in 10, 100 and 1000 m³ vessels

Initial pressure	10 m ³			100 m ³			1000 m ³		
	Baker	Prugh	TNO	Baker	Prugh	TNO	Baker	Prugh	TNO
100	29	25	45	63	54	90	106	118	156
50	23	19	40	49	41	88	83	88	140
25	18	14	35	39	30	75	66	65	120
10	13	9	30	28	20	64	47	43	102
5	10	6	26	21	14	56	36	31	89

According with the presented calculations, i.e. with the more conservative approach of the TNO's method, the threshold distances calculated by this procedure always provide larger distances with respect to the Prugh's ones, by a 40 % average and 30% average with respect to the Baker's, respectively (see Table 2). If the same analysis is carried out for the larger vessels (100 m³ cylindrical and 1000 m³ spherical), it can be found that the above considerations apply as well, the differences between the two approaches being even more apparent, since the overpressures calculated by the Baker's method are always higher than Prugh's ones, independently on the initial pressure and in the whole range of distance analyzed. Also for the threshold distances, the difference is more apparent for the large vessels than for the small one, since the values provided by the Baker's method are more than double those calculated by Prugh's one (see Table 2) for the 100 m³ cylindrical tank and about 80 % in the case of the 1000 m³ spherical one.

Summary

This paper presented preliminary studies on the potential of BLEVE overpressure hazard. The magnitudes of the forces which are generated in a pressure vessel containing ammonia have been calculated. Even do-how manuals produced by coordinating agencies – such as Netherlands Organization for Applied Scientific Research and the Centre for Chemical Process Safety – describe different consequence assessment methods with little commentary on their relative merits. Due to the fact that industry and regulatory agency used legitimate consequence analysis model risk assessment conducted by an industry and a regulatory agency may differ widely from each other. The study cases demonstrate that the two most used simplified methods for estimating the trend of overpressure vs. distance in case of gas explosions give rise to rather different profiles in the near field, which become closer in the far field, where the absolute values are lower. From this point of view, the results are particularly interesting at distances in the range of the usual equipment spacing. Baker's method estimates are invariantly more conservative: the observed differences are also function of the initial pressure, of the vessel size and of the substance under exam.

Conclusion

Theoretical investigations of three methods for calculating the physical effects of explosions of vessels containing pressurized liquids have been carried out with several volumes (10 m^3 , 100 m^3 and 1000 m^3) and burst pressures of the vessel (100 kPa, 50 kPa, 25 kPa, 10 kPa, 5 kPa). Overpressure profiles calculated with both methods are closer for Baker's and Prugh's method than for more precise TNO's method. It can be concluded that both models can be used to estimate, with reasonable accuracy, the overpressure field at a certain distance from the explosion center, while their simplifying assumptions do not allow getting reliable values close to the vessel. In such cases Baker's method can be used for rough estimates, but where accurate data are needed, more sophisticated techniques such as TNO's model should be used.

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References

- [1] T. Abbasi, S.A. Abbasi, The boiling liquid expanding vapour explosion (BLEVE): Mechanism, consequence assessment, management, J. Hazard. Mater. 3 (2007) 489-519.
- [2] R.W. Prugh, Quantitative Evaluation of BLEVE Hazards, 22nd Loss Prevention Symposium, American Institute of Chemical Engineers, New Orleans, USA, 1988.
- [3] W.E. Baker, P.A. Cox, P.S. Westine, J.J. Kulesz and R.A. Strehlow, Explosion Hazards and Evaluation, Elsevier, New York, 1983.
- [4] R. Bubbico, B. Mazzarota, Analysis and comparison of calculation methods for physical explosions of compressed gases, Chem. Eng. Trans. 32 (2013) 133-138.

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