Modelling of Corrosion Damage of Real Aircraft Structure

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Abstract

A software analysis of corrosion damage of construction detail of new developed aircraft was carried out. The analysis was done by BEASY Corrosion Manager software. This software was developed for modelling of galvanic corrosion under the conditions of thin film of electrolyte. Critical input for the modelling are polarization curves measured in thin film. Corrosion cell for measuring in thin film was developed and the polarization curves of used materials were measured. In addition, experiments in corrosion chamber were performed to compare the software analyses with experimental results. To evaluate the experiments, gravimetric analysis and corrosion profiles measuring was used. As a result of corrosion software analyses, 3D maps of potential, corrosion current, corrosion rate and mass loss rate was calculated. The corrosion analysis is a useful tool for corrosion damage prediction, but it is necessary to improve the technique of polarization curve measurement and make the setting of film thickness and electrolyte conductivity in the model more precise.

1. Introduction

Corrosion is a process when technical materials return into their, from thermodynamic point of view, more stable state and this process is unavoidable. Aim of technical solution is to minimize the rate of corrosion processes of all structural parts in a construction. Corrosion has many forms, one of which is galvanic corrosion. Galvanic corrosion takes place, when two electrically conductive, electrochemically different materials come in mechanical contact in a presence of an electrolyte. Modern machinery and the aircraft industry especially use a lot of different construction materials in order to achieve desired combination of mechanical parameters, weight, temperature stability and so on. This combination of materials, even today very often metallic materials, involves a risk of development of galvanic corrosion. Today technical practice of galvanic corrosion risk determination relays on tables of corrosion potentials. For each material involved in particular construction must be found the value of corrosion potential in expected corrosion environment. From the ratio of surface areas of the materials it is than possible to estimate the corrosion risk. When there are more difficult geometries and space arrangements, or combinations of more than two materials are used, the situation becomes very complex. Solving of such detail from the corrosion point of view is a matter of experience or it is necessary to carry out time consuming and expensive experiments.

This paper deals with the possibilities of software simulation of galvanic corrosion damage.

Galvanic corrosion is not only a problem of situations with a presence of large amount of liquid electrolytes as for example water tanks, pipelines or ship hulls. Galvanic corrosion occurs even in atmosphere. In “dry” air, the electrolyte is present as a layer of adsorbed moisture. In more wet atmospheres, the condensation can occur. And in the aerospace field, water from rainfalls is periodically presented on the upper parts of the fuselage.

In this paper, specialized software is used for the simulation. A special assumption is done in this software about a thin layer of electrolyte. This assumption means that the thickness of the layer is order of magnitude smaller than any distance of two different materials interfaces in the solved construction. This assumption is often satisfied with no doubt in a case of moisture adsorption. In a case of condensation or when liquid water stationary or running off the construction is presented, the situation should be checked more carefully. The assumption of a thin electrolyte layer has consequences in a way, how a material behaves in a presence of such electrolyte. Among others, the thickness of the electrolyte layer influences the value of the corrosion potential [1-3].

2. Software description

Software BEASY Corrosion Manager (Beasy CM) (CM BEASY Ltd., UK) was used for the simulation. The programme is designed to model a construction and a layer of electrolyte covering the construction and to simulate the galvanic contribution to a total corrosion attack. In a vicinity of different material interfaces, this contribution is a prevailing factor of total corrosion damage.

It is intended as a helping tool for mechanical engineers and designers with no broad technical or even scientific background in the field of corrosion. The programme is able to load standard 3D geometry formats of engineering constructions. After adding further input data regarding the corrosive environment, the programme is able to depict critical details with high risk of corrosion and model the distribution of corrosion rates. Already during the design stage of a new construction there is a possibility to check the corrosion aspect of the assembly.

Described software contains some simplifications in the physical model of the galvanic corrosion based on the assumption of thin electrolyte layer (TEL). The simplifications bring significant lowering of computational demands. On the other hand, the simplifications bring a demand of specific form of input data. Additionally, meeting of the TEL assumption is a necessary condition for a right result of the simulation.

2.1 Software theory

Each metal in an electrolyte has a unique potential called corrosion potential E_{corr}. The value of E_{corr} is given by combination of the metal and the electrolyte. If two different metals are connected in the electrolyte, the potential difference causes an electrical current, corrosion current I_{corr}, floating between the metals. The metal with lower value of E_{corr} becomes an anode and corrodes. The electrically more noble metal with higher value of E_{corr} becomes cathode. The cathode does not corrode but more complex depolarization processes take place on its surface. Electrical circuit closes through the electrolyte. The current floating through the interface between the metal and the electrolyte changes the value of metal E_{corr}. The relation between the corrosion current density j_{corr} (I_{corr} per unit area) and the potential E_{corr} is represented by polarization curve. I_{corr} is bound with a corrosion rate v_{corr} by a Faraday's law of electrolysis.

The scheme of galvanic corrosion under thin film of electrolyte is in Figure 1.

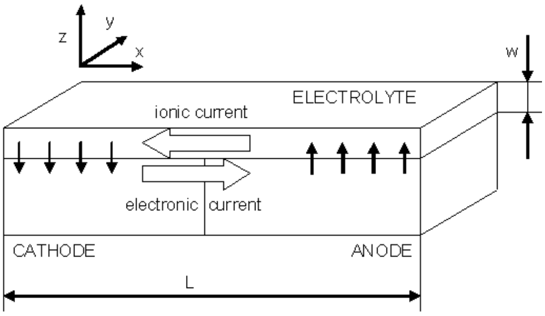

Figure 1: Galvanic corrosion under a thin film of electrolyte, w«L

Solved equation is the charge conservation equation under steady state in the volume of the electrolyte:

$$\nabla \vec{j} = 0 \tag{1}$$

The boundary conditions for the surface of the anode and of the cathode are described by the corresponding polarization curves for the metal of the anode and for the cathode respectively. These polarization curves must be contained in the input data for the simulation.

Furthermore, in used software the assumption about TEL is mathematically treated. If the thickness of the electrolyte w is much smaller than the characteristic dimension of the problem L (see Figure 1), the electrical potential in the electrolyte can be considered as constant in the direction perpendicular to the electrode surface (z direction). This allows not finding the solution of the charge conservation equation in the whole volume of the electrolyte. The solution must be found in two directions parallel with the electrodes surface (x and y direction). In the z direction it is possible to do direct integration of the z component of current density j_z along the thickness w. The assumption about TEL brings a lowering in dimensionality of the problem from 3D to 2D. The effect of the charge exchange between the electrode and the electrolyte is presented as a source term instead of as boundary condition.

As the TEL assumption is an integral part of the solution of used mathematical model, it is necessary to judge each situation to be solved from this point of view. In addition, polarization mechanisms are different in the presence of TEL in comparison with the bulk electrolyte. The thickness of TEL has direct impact on the measured polarization curves. Therefore it is necessary to measure polarization curves in layers with thicknesses similar to those, which are presented during the exposure. Polarization curves have to be measured in electrolyte with identical or similar composition as the electrolyte presented during the exposure.

Further, input data of the mathematical model have to contain the value of electrolyte conductivity and the TEL thickness.

2.2 Model editing

Corrosion is a matter of material surface. There is a possibility to create a new geometry in a preprocessor, which is GiD (CIMNE, Spain), consisting just of surfaces. Most common situation is to import an existing geometry. Import is possible in following formats: IGES, DXF, Parasolid, ACIS, VDA, Rhino or Shapefile. It is possible to import mesh as well in following formats: NASTRAN mesh, SRL mesh, VRLM mesh, 3D Studio mesh, CGNS mesh, Surface mesh and VTK Voxels. In a case of imported geometry, it is necessary to edit it in the preprocessor in the way that the geometry comprises only the surfaces, which are exposed to the corrosive environment. All surfaces, which are included in the geometry prepared for the modelling, must have assigned parameters of the TEL and are included into the calculation. This requirement claims to remove all internal surfaces of imported geometry. Because the software does not solve crevice corrosion, it is necessary to remove all very close parallel surfaces, which are contained for example in sleeve bearings. Editing of a geometrical model and its preparation in preprocessor GiD for the simulation via BEASY CM is shown in the Figure 2.

Figure 2: Editing of bolt, nut and washer (a) and their assembly (b)

There is a possibility in the software to model an influence of coatings, typically paints. Effect of paint is in the model described by two variables. First is the breakdown factor describing the ratio of damaged surface area to the total surface area of concerned surface. For a perfect coating the value of breakdown factor equals zero, for a coating, which is totally scraped off, the value is 1. Second variable characterizing the coating is its ohmic resistance. Effect of a coating in the model is restriction of flowing corrosion current between the surface and the electrolyte. For a material with an electrochemically active coating, e.g. galvanic coating, it is necessary to measure new polarization curve.

2.3 Outputs

Outputs of the simulation are represented by potential, corrosion current, corrosion rate and mass loss rate distribution over the surface of solved construction. Potential distribution is given by the values of corrosion potentials of involved materials in present electrolyte, by their polarizability and by the sheet resistance of present TEL. The last quantity is given by conductivity of the electrolyte and by the thickness of the layer. Corrosion currents floating through the TEL together with the sheet resistance cause continuous distribution of electrical potential in lateral direction of the layer. Corrosion current distribution is bound with the potential by the polarization mechanisms. This binding condition is for each material described by corresponding polarization curve. Positive value of corrosion current represents corrosion, dissolving of the material into the electrolyte in a form of positively charged ions. Negative value of corrosion current represents not the corrosion but depolarization processes, in which very often the atmosphere takes part. This is one of the reasons, why the thickness of the TEL influences the shape of measured polarization curves. Corrosion currents are expressed as current densities.

Simple and clear representation of the simulation results is the corrosion rate and the mass loss rate. These values are connected with the corrosion current by the Faraday's law of electrolysis. Corrosion rate represents dimension changes during time, whereas the mass loss rate represents the weight changes during time. The units used in the software are [mpy] (mils per year) for corrosion rate. For the conversion to SI units an equation 1 mpy = 0.0254 mm/year is applicable. For the mass loss rate the used units are [g/(day·m^2)].

3. Experimental procedures

There is no comprehensive study of polarization behavior of technical materials in TEL for different electrolytes in the literature. This is because broad variety of materials and almost infinite amount of electrolyte compositions and layers thicknesses. Measured polarization curves are the critical input for the simulation. A method for measurement of polarization curves in TEL is under development in Aerospace Research and Test Establishment. First curves, used in current study, were measured in cooperation with Institute of Chemical Technology, Prague. In addition, a comparison was done between the simulation and corrosion test in neutral salt spray chamber.

3.1 Polarization curves measurements

For the measurement in TEL, special corrosion cell was designed. A scheme of the cell can be seen in the Figure 3, together with a photo of the realization. The cell uses three electrode system. Working electrode was the measured material and the active surface area of the sample was defined by a silicone rubber. Glass beads were fastened in the rubber holding the counter electrode from Pt wire at the same time (see Figure 3). The reference electrode Ag/AgCl (1M KCl; E = +236 mV at 25°C) with a small tip was utilized and was immersed directly into the TEL. Measured area of the sample has to be flat, but in general, this arrangement can be used for measurement on a sample of arbitrary shape. A differential weighing was used to determine the weight of electrolyte on the working electrode and the thickness of the TEL was calculated from the geometry and the density of used electrolyte. Thickness about 1mm was reached with described arrangement. Potentiostat Reference 600 (Gamry Instruments Int., USA) was used to measure the curves with software Gamry Framework 5.21.

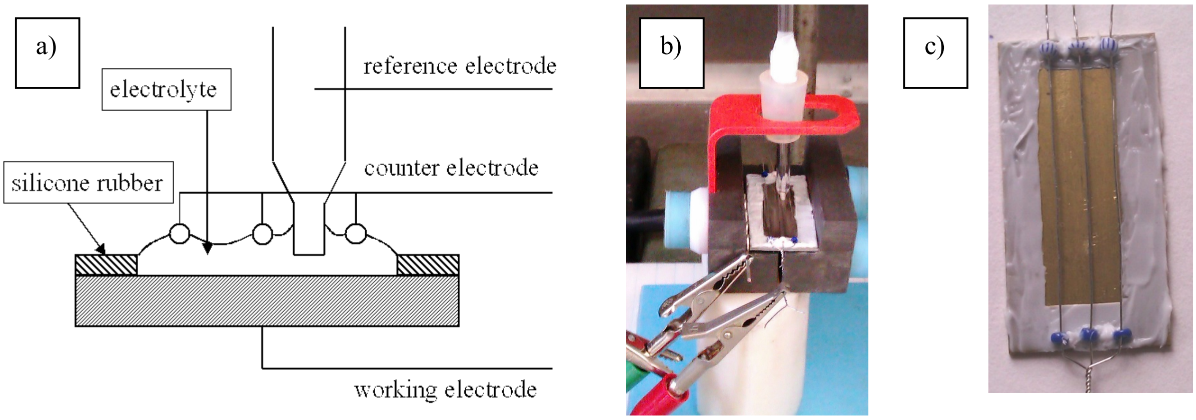

Figure 3: Corrosion cell: the scheme (a), the realization (b), detail of working and counter electrode (c)

Two electrolytes were investigated, 1 M NaCl aqueous solution and tap water. Polarization curves in NaCl solution were measured to carry out comparative experiments in salt spray chamber. Tap water, which undergoes no special purification treatment as e.g. distillation, was chosen as a substitute for electrolyte covering real constructions in case of adsorption or condensation of moisture. Although the water coming from vapour phase is pure, the surface of constructions is never absolutely clear. Characterization of the two electrolytes is given in Table 1.

Table 1: Characterization of electrolytes

Electrolyte	**Conductivity [S m^{-1}]**	**pH**
1 M NaCl	8.6000	6.10
Tap water	0.0445	7.36

3.2 Comparative experiments

For the comparison between the simulation and the experiment the simplest geometry of two square plates joined by their edges was implemented (see Figure 4). Metal sheet samples of thickness 1 mm and dimensions 100 x 100 mm^2 was mechanically connected side by side by a both-sided adhesive tape. Electrical connection was realized on the rear side of the plates by means of a conductive adhesive tape (ElchemCo, CZ) together with mechanical strengthening by an insulating underlayment. These corrosion couples were exposed to neutral salt spray according to ČSN EN ISO 9227 standard for 96 hours. Used combinations of materials are listed in Table 2.

Table 2: Corrosion couples

Mild steel / Stainless steel
Mild steel / **Galvanized iron**
Mild steel / **Aluminum**
Stainless steel / **Galvanized iron**
Stainless steel / **Aluminum**
Galvanized iron / Aluminum

Note: anodic member of each couple is typed bold

Two methods were used to do the comparison. One of them was gravimetric analysis. Corrosion couples were exposed to salt spray together with one sample of each material standing alone. These samples were used to determine the rate of uniform corrosion caused by aggressive corrosion environment. After the exposure, corrosion products were removed and weight loss was determined for each sample. Loss of weight of each sample from corrosion couple was diminished about the weight loss of sample from the same material standing alone. In this way, the influence of uniform corrosion was separated. On the side of the simulation, integral value of corrosion current for each sample was used to determine the total charge, which has floated through the surface during the 96 hours of exposure. Weight loss in the simulation was calculated from the Faraday's law:

$$m = \frac{EW.I.t}{F} \tag{2}$$

where m [g] is the weight loss, EW is the dimensionless equivalent weight of the material, I [A] is the integral corrosion current of the whole sample area, t [s] is the time of exposure and F [C·mol^{-1}] is the Faraday constant. Values of equivalent weights were taken from literature [4].

Figure 4: Corrosion couple stainless steel/aluminum (masked for the profile measurements) after the exposure (a), profilometer T1000 (b)

The second method to compare simulation and experiment was measuring of corrosion profiles. Each corrosion couple was partially covered with two stripes of adhesive tape (see Figure 4). After the exposure and the corrosion products removal the depth of corrosion was measured as a function of the distance from the material interface. Profilometer T1000 (Hommel-Etamic) was used to measure the depth of corrosion trench. The depth of corrosion far from the interface (the limiting value) was subtracted from the total depth of corrosion, because this was again the influence of uniform corrosion. On the side of the simulation, distribution of corrosion rate was recalculated as a distribution of corrosion depth and the comparison was done graphically.

Two thicknesses of the TEL was modelled, 0.1 mm and 1 mm, because the layer of electrolyte in the corrosion chamber is not homogenous.

4. Results

Results can be divided into three thematic groups. The first group is represented by measured polarization curves. It is very advantageous to have a possibility to measure polarization curves in TEL and to develop a polarization database on the basis of real solved tasks. In this paper a representative set of measured materials used in presented simulation is shown. The comparison between the simulation and experiment is the second topic of this contribution. The main theme of this paper is the corrosion software analysis of a real aircraft structure.

4.1 Polarization curves

Measured polarization curves in 1 mm thick layer of 1M NaCl electrolyte are shown in the Figue 5 and the curves measured in 1 mm thick layer of tap water are shown in the Figure 6. Characteristic values determined from measured curves for each material in the different electrolytes are given in Table 3. These values are free corrosion potential, free corrosion current density and free corrosion rate, which are determined from the slope of polarization curve in the so-called Tafel regions. The differences of electrochemical behavior of each material due to electrolyte of different composition are apparent from the figures and the table

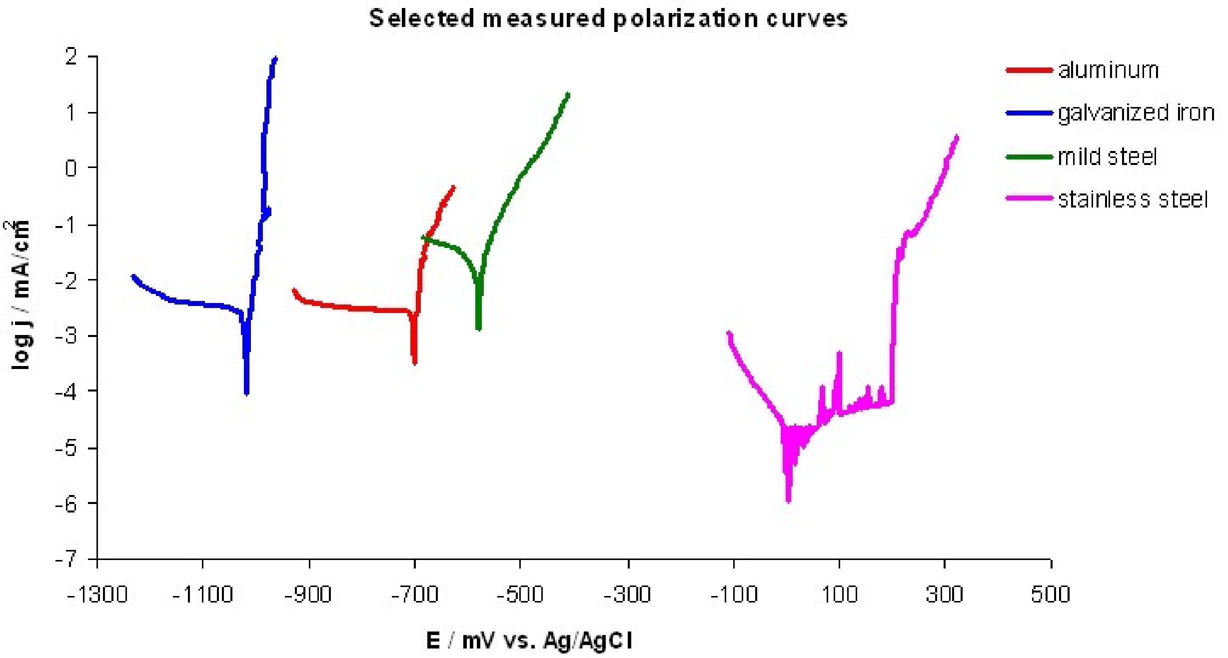

Figure 5: Measured polarization curves: TEL of 1M NaCl, 1 mm thickness

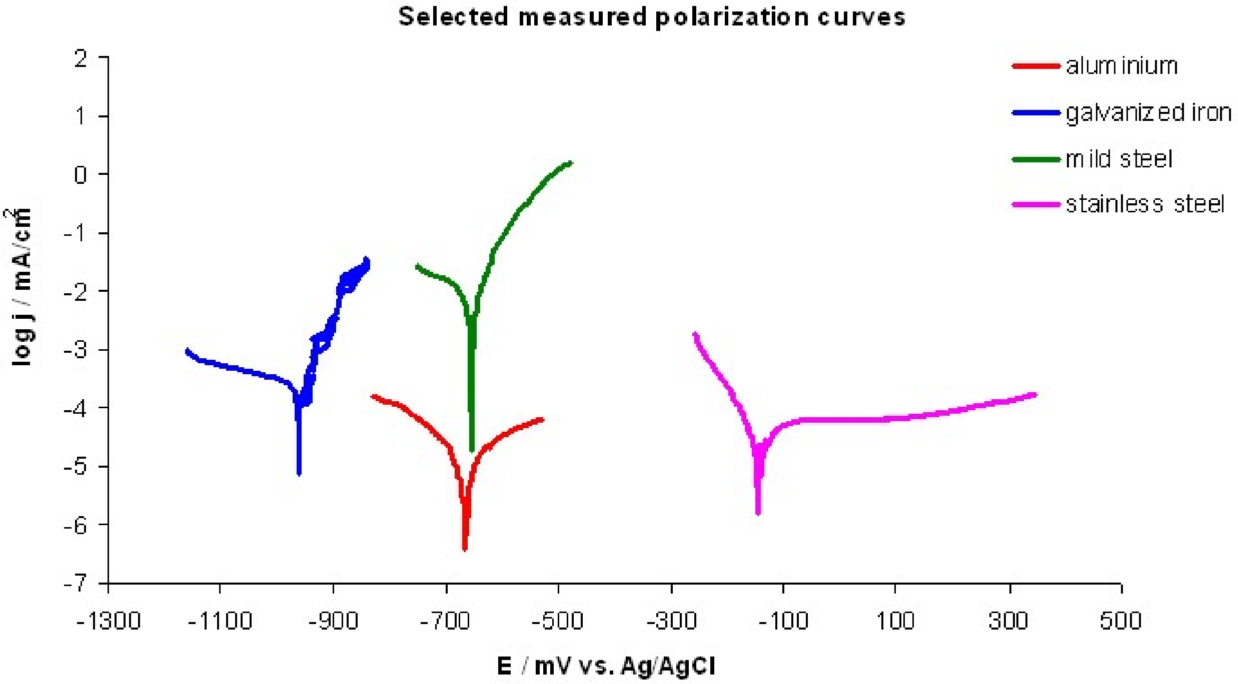

Figure 6: Measured polarization curves: TEL of tap water, 1 mm thickness

Table 3: Values detrmined from polarization curves in 1 mm thick TEL

	1 M NaCl			**Tap water**		
	E_{corr} [mV]	**j_{corr} [mA cm^{-2}]**	**v_{corr} [mpy]**	**E_{corr} [mV]**	**j_{corr} [mA cm^{-2}]**	**v_{corr} [mpy]**
Mild steel	-579.7	0.0223872	0.25987	-653.8	0.0089125	0.10346
Stainless steel	38.0	0.0000251	0.00026	-146.6	0.0000398	0.00041
Galvanized iron	-1017.2	0.0033884	0.05083	-959.3	0.0002512	0.00377
Aluminum	-702.4	0.0026915	0.02921	-665.4	0.0000170	0.00018

4.2 Comparative experiments

Comparison between the experiment and the simulation by means of gravimetric analysis can bee seen in Table 4. The table shows experimentally determined weight loss caused by a galvanic corrosion on the anodic member of each corrosion couple. Two values of weight loss are given in the table for the simulation. One value was calculated for a model with a thickness of TEL 0.1 mm and the second one for a model with a thickness of TEL 1 mm.

Table 4: Measured and modelled weight loss

Anodic member (second sample in corrosion pair)	**Experiment [g]**	**Model (0.1 mm TEL) [g]**	**Model (1 mmTEL) [g]**
Mild steel (Stainless steel)	0.026	0.106	0.231
Galvanized iron (Mild steel)	0.000	0.244	0.778
Galvanized iron (Stainless steel)	0.004	0.220	0.499
Galvanized iron (Aluminum)	0.065	0.078	0.167
Aluminum (Mild steel)	0.047	0.028	0.089
Aluminum (Stainless steel)	0.020	0.042	0.100

Comparison between the experiment and the simulation via corrosion profiles measurement was possible only for the aluminium samples. On mild steel and galvanized iron samples, the influence of uniform corrosion was much greater and has overlaid the influence of galvanic corrosion. On stainless steel, the rate of both uniform and galvanic corrosion was so low, that after four days of exposure it was not possible to measure any corrosion profile.

Corrosion profiles measured on aluminium samples, which were anodes in their corrosion couples, are shown in the Figure 7 and in the Figure 8. Each figure shows measured corrosion profile and simulated profile for the thickness of TEL 0.1 and 1 mm.

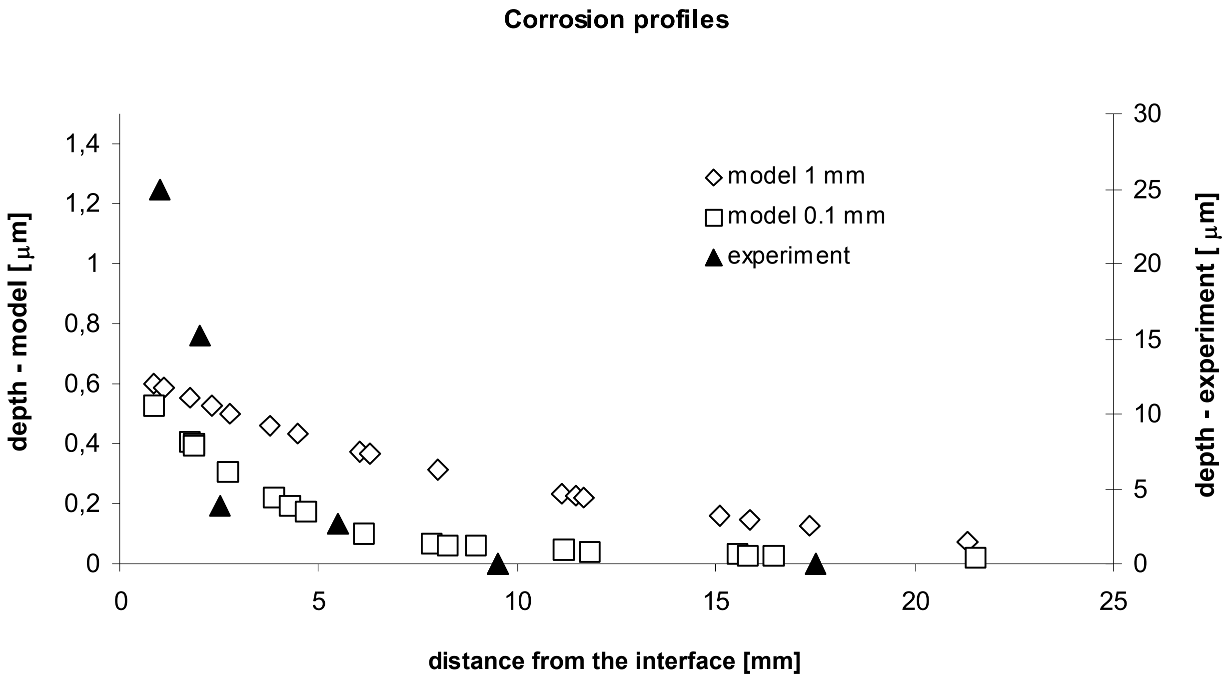

Figure 7: Measured and simulated corrosion profile on aluminum anode – aluminum/mild steel couple

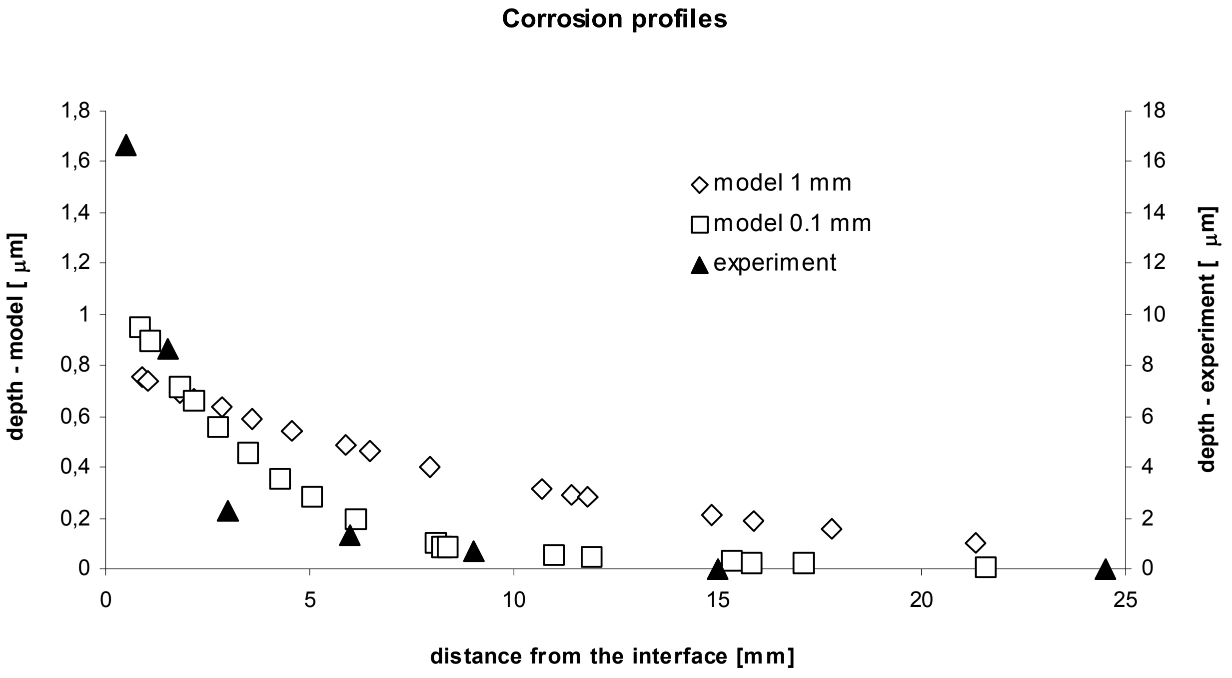

Figure 8: Measured and simulated corrosion profile on aluminum anode – aluminum/stainless steel couple

4.3 Corrosion damage

Solved construction detail was represented by an attachment of hydraulic cylinder of nose landing gear to the fuselage. The structure is shown in the Figure 9 together with material composition. Corrosion attack by the atmospheric corrosion was simulated. Influence of atmosphere with two different values of relative humidity (RH) was investigated by means of the simulation. According to the literature [5], two different thicknesses of adsorbed moisture layer were modeled, 100 μm for the 90% RH and 10 μm for the 60% RH.

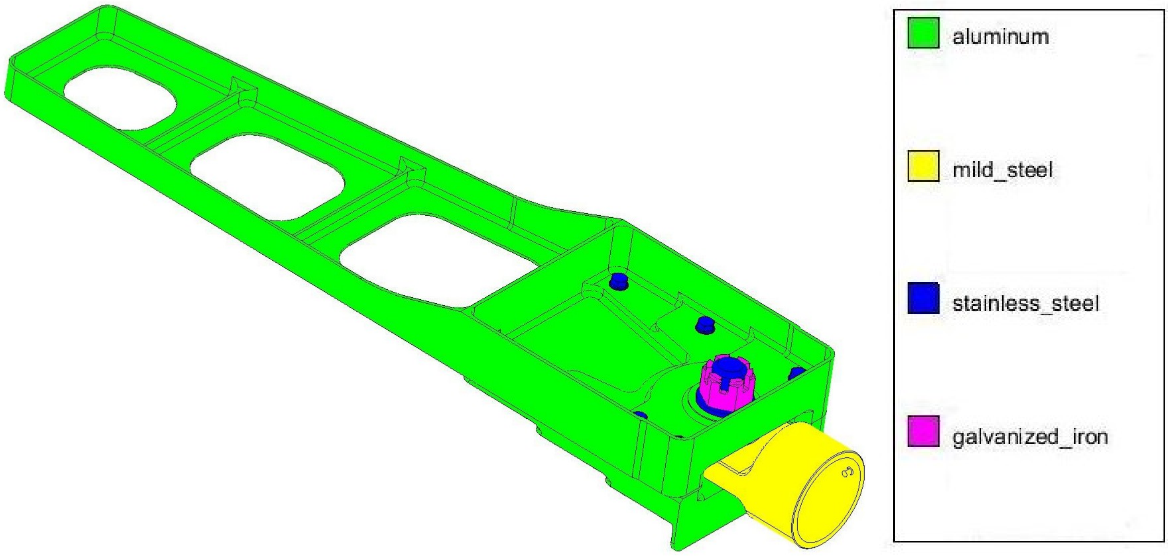

Figure 9: Solved construction detail

The difference in the potential distribution is shown (see Figure 10). The distribution in the thicker layer is more continuous. The mutual influence of different materials has longer range. In the thinner layer, potential of each material approaches the free corrosion potential of the material faster in dependence on the distance from the material interface.

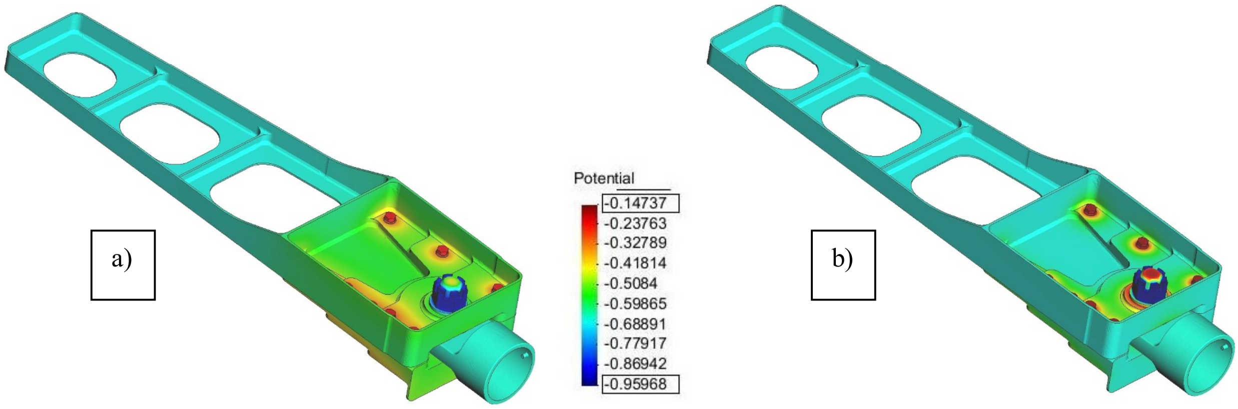

Figure 10: Modelled potential distribution. Atmosphere with 90% RH (a) and 60% RH (b)

Corrosion current density distribution is shown in the Figure 11. Trends in the current density distribution are the same as of the potential distribution. Current density is bound to the potential by the polarization mechanisms. Only positive current density represents corrosion.

Corrosion rate is shown in the Figure 12. This quantity shows in a simple and clear way the risk and the magnitude of corrosion attack. Corrosion rate is bound to the current density by Faraday's law of electrolysis. Trends in corrosion rate distribution are the same as of the potential and current density distribution. Maximum corrosion rates are at the galvanized iron nut/mild steel bolt interface. Modelled value on the nut is 0.6491 mpy (0.0165 mm/year) in the atmosphere with 90% RH and 0.55386 mpy (0.0141 mm/year) in the atmosphere with 60% RH. Second problematic contact is between the galvanized nut and the stainless steel washer. Here the maximum modelled corrosion rate in the atmosphere with 90% RH is about 0.1 mpy (0.0025 mm/year). Other connections have significantly lower corrosion rates.

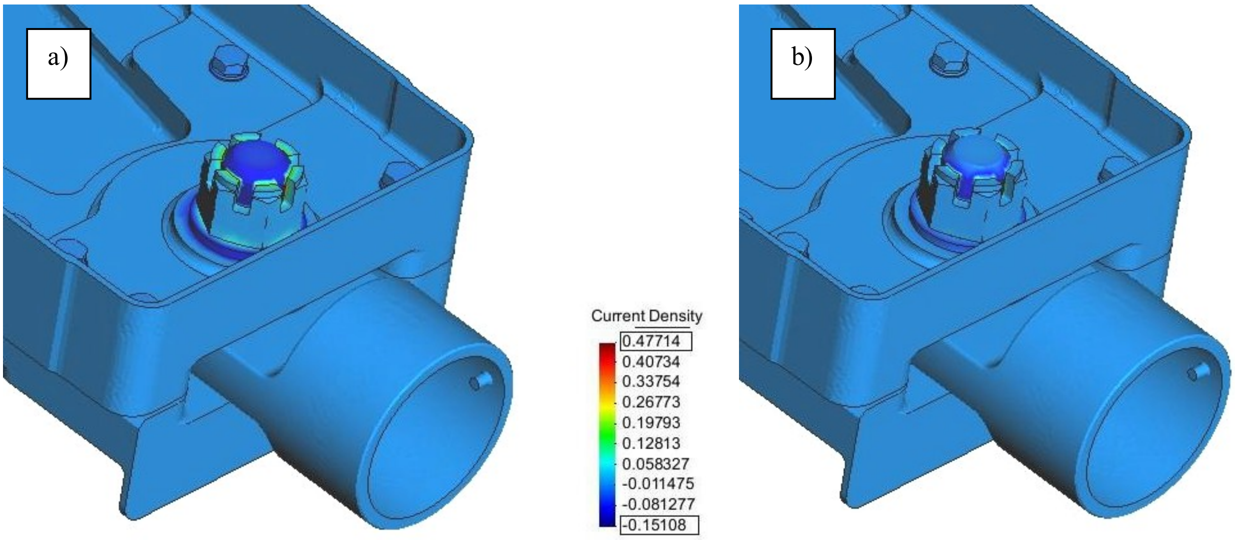

Figure 11: Modelled corrosion current density distribution. Atmosphere with 90% RH (a) and 60% RH (b)

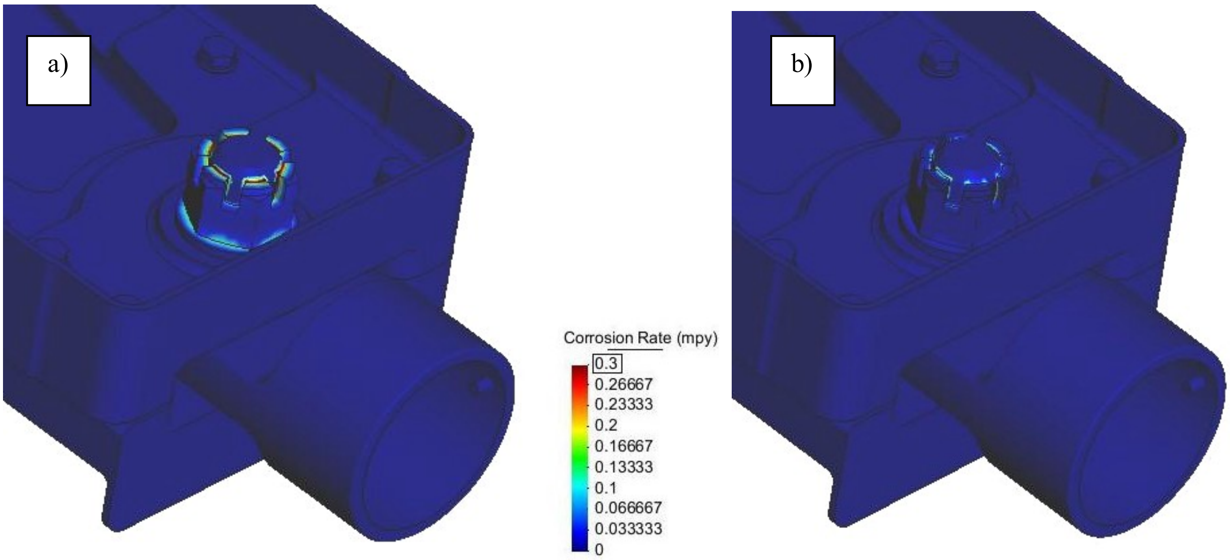

Figure 12: Modelled corrosion rate distribution. Atmosphere with 90% RH (a) and 60% RH (b)

5. Discussion

BEASY Corrosion Manager is designed to model the corrosion in TEL. From the showed description it is obvious, that the whole solved geometry is considered as a 2D problem. Relative position of individual surfaces is described in the input data by means of common lines. If two surfaces of real structure are parallel and very close, they can create a crevice filled up with the electrolyte. In this situation, the two surfaces influence each other electrochemically very intensively. Crevice corrosion takes place in this arrangement. An example of such situation can be two metal sheets, not perfectly even, riveted together. Used software does not solve crevice corrosion. The way to treat such details of solved construction in the model is to assign thick layer of electrolyte to the surfaces forming the crevice. The calculated sheet resistance of TEL in the crevice is then low and the two surfaces influence each other electrochemically very intensively as in the real situation.

Used technique of polarization curves measurement is very important. According to literature, the TEL thickness influences measured curves strongly when the thickness is 500 μm or lower [6]. The technique described in this work has main disadvantage in the capillary action of Pt wire counter electrode and reference electrode. So the thickness of measured film is not constant all over the working electrode. The second disadvantage is the surface tension of measured electrolyte. The force of the surface tension does not allow to measure films much thinner than 1 mm (achieved minimum thickness was about 0.7 mm). The problem can be partly avoided by using surfactants, but this approach changes the composition of measured electrolyte. Because of the influence of the TEL thickness, it is necessary to measure curves in thinner films to model especially atmospheric corrosion properly (thickness of TEL in order of magnitude 100 μm).

In principal, it is possible to measure polarization curves in electrolyte of any chemical composition. The main issue is the composition of the electrolyte covering real structures. Critical variable is the electrical conductivity. When adsorption or condensation or presence of rainfalls is considered, the concentration of any specific chemical is not assumed in prevailing amount. The main origin of electrical conductivity of such electrolytes is the surrounding atmosphere. The atmosphere is even more important in the case of TEL than in a bulk electrolyte. When specific pollutant is expected in the atmosphere, it is possible to simulate its influence in the laboratory conditions in a closed system. Simulation of the corrosion in TEL of specific chemical solution is possible after measuring of polarization curves in the solution. Typical example is the salt solution used in the comparative experiments.

Quite disputable is the thickness of TEL in real situations. The thickness as a part of input data influences the value of the sheet resistance of the layer. Impact of the modelled thickness is significant, as can be seen from the results of corrosion damage simulation. Very thin layers of adsorbed moisture are not measurable with standard laboratory equipment. Often used technique of thickness measurement of thin layers is the optical ellipsometry. Among corrosion engineers, such sophisticated methods are not common so far, and the easiest way to determine the thickness of adsorbed layer is to search in the literature. Thicknesses of condensed layers are accessible to measurement in an easier way, for example by means of confocal sensors. Moreover, a calculation approach is possible [7]. In case of rainfalls, the thicknesses are even larger and the measurement should be uncomplicated. In general, there is a need to know thicknesses of TEL in typical situations, because simulations of constructions in stage of development are assumed. Similar to the development of polarization curve database, a database of typical electrolyte thicknesses is to be established, with advantage on the basis of solved case studies and supported by corrosion experiments. Similar situation is with the values of electrolyte conductivity.

Achieved results of comparative experiments have confirmed only qualitative agreement between the simulation and the experiment. Problem of the simulation was polarization curves measurement technique with the above-mentioned disadvantages and setting of the layer thickness in the model. Gravimetric analysis includes the whole surface of the samples. Here the simulation gives higher corrosion rate for the 1 mm thick layer and even for the 0.1 mm thick layer except the corrosion couple aluminum/mild steel. The conclusion is, that thinner layer should be modelled. Results of corrosion profile measurement suggest, that thinner layers should be modelled as well. The influence of thinner modelled layer is especially clear from the Figure 9 – higher rates at the material interface and shorter range of the corrosion. But there is still large mismatch between modelled and measured profile. After the initiation of galvanic corrosion, formed trench in the anodic member of the corrosion couple changes the thickness of TEL in the vicinity of material interface. Together with arising corrosion products, the corrosion near the material interface continues in changed conditions. During validation of physical model of this software, total corrosion current between aluminum and carbon fiber reinforced plastics electrodes was measured before the formation of the corrosion trench with good agreement with the simulation [7].

6. Conclusions

Software analysis of corrosion damage of construction detail of new developed aircraft was carried out. The highest corrosion damage is on galvanized nut, maximum modelled corrosion rate is 0.6491 mpy (0.0165 mm/year) in the atmosphere with 90% RH and 0.55386 mpy (0.0141 mm/year) in the atmosphere with 60% RH.

Rather new software was used and the input data for the simulation was measured. A method for polarization curves measurement was developed, which is to be further improved. At state-of-the-art, corrosion damage risk and critical parts detrmination is possible with good reliability. Determination of absolute values of corrosion rates needs better setting of thickness and conductivity of electrolyte layer in the model of each individual solved situation.

Acknowledgements

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