ABRASIVE WEAR OF HOT-DIP GALVANIZED MULTILAYER COATINGS

Thesis of the doctoral (Ph.D) dissertation

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1. INTRODUCTION, GOALS

1.1. Actuality of theme

The hot dip – galvanizing is a technology used to protect durably the surfaces of iron – and steel constructions which protective effect depends strongly on the thickness and density of the surface layer. Its suggested main fields of application are the surface protection in every corrosion class at atmospheric load as well as the surface protection of metal constructions of ventilated insides. Its application spreads continuously because of the reliable protective effect of the coating, the industrial scale applicability of the process, comparatively high productivity and because of small labour requirement.

Ever increasing proportion – more than 6 million metric ton – is supplied with hot-dip galvanized coatings of the constructions manufactured in Europe. Mechanical loads also effect the products beside corrosive effects at industrial, agricultural and public pavement grids, at industrial filters which means spreading and at the same time new application fields. Nowadays it is already a utilizing demand to develop abrasion and rubbing resistant coatings at hot – dip galvanized surfaces exposed to abrasion, to sand – and breakstone scatter. Adhesive sliding conditions and deformation capacity have been studied in case of comparatively limited conditions but regulated comparative measuring data concerning abrasive resistance there aren’t at disposal neither in technical literature nor in the database of coat – producing and of developing companies. These data are indispensable to develop technology improving the abrasive resistance.

1.2 The aim and tasks of the research work

The aim of the research work was to determine with rapid comparative laboratory abrasion tests that the hot-dip galvanized coatings with different composition what abrasive resistance got as compared to each other. To carry out tests based on such measurings which represent by properly scientifical sound foundations the differences between the abrasive resistance of coatings hot-dip galvanized having different compositions. My further aim is to present empirical properties in the function of frictional length, speed and the pressure of abrasive medium for developing technologies improving abrasive resistance.

It can be further established from studying the technical literature that research and development carried out in the well separated progress periods of more than 200 year of technology haven’t cleared the abrasive condition of the coated layer. Based on the revealed shortcomings my research tasks are the followings:

- to study and to select types of coatings used surfaces exposed to abrasive load, to make and to coat specimens,
- analysing the coating, to determine exact data (geometric, layer structure, composition characteristics),
- to develop abrasion tester, to select abrasive medium and to determine the measuring system and method,
- to carry out series of tests after pre-test, to elaborate measuring data and graphic performance,
- to reveal connections, conclusions.
2. MATERIAL AND METHOD

The aim of my research work was to determine with rapid comparative laboratory abrasion tests that the coatings with different composition hot-dip galvanized what abrasion resistance got as compared to with each other. Mechanical loads also affect the products beside corrosive affects at industrial, agricultural and public place pavement grids at industrial filters hot-dip galvanized spreading nowadays. It is already a utilizing demand nowadays to develop an abrasion and rubbing resistance coatings at surfaces hot-dip galvanized exposed to abrasion, to sand- and breakstone scatter. There are not at disposal neither in technical literature nor in database of coat-producing and of developing companies comparative regulated measuring data concerning abrasion resistance. These data are indispensables to develop technology improving the abrasion resistance.

Based on the producer’s recommendations the Technigalva® and its modified variation by heat treatment - Technigalva® H-coatings were tested. The achieved results help the further layer development using heat treatment technologies to modify the multilayer structure.

2.1. Coated specimens tested

We have chosen S235JRG2 steel as specimen material used for abrasive tests, which is the most definite base metal for example of pavement grid. As this material is desoxidized with aluminium- and not with silicium – and the mechanism of layer developing is determined first of all by the amount of silicium to be in steel, therefore it can be hot-dip galvanizing outstandingly. We have taken into account at deciding the specimens dimension the tool form of the abrasion tester, as well as those positions and the geometrical dimension of the container containing the abrasive medium ensuring abrasion. Figure 1 shows the dimension of specimen galvanized.

![Figure 1. Specimen dimensions](image-url)
Two types of coating were tested in the function of friction length, speed and pressure of abrasive medium.

- Technigalva: The determining components are the zinc (Zn), aluminium (Al), lead (Pb) and nickel (Ni) of the zinc-bath. The coating was made by dry periodic technology.

- Technigalva heat treated: The specimens were heat treated in order to the coating should have zinc-iron alloy phases in the total cross-section.

The abrasion resistance of coatings depends on its hardness, therefore it is needed to measure the micro-hardness. The micro-hardness tests showed that the Techigalva coatings had 48 HVM in average, while the heat treated coating had 106 HVM in average. The testing points on the specimen’s surface can be seen in figure 2. We have selected 10 – 10 test specimens and after measuring each one the registered hardness values were averaged that are summarized in table 1.

Reference Technigalva coatings resulted in average: HV M: 47,1 while the range: $R_{\text{max}} - R_{\text{min}} = 54 - 41,7 = 12,3$

The heat treated Technigalva resulted in average: HV M: 106,6 while the range: $R_{\text{max}} - R_{\text{min}} = 114,2 - 89,5 = 24,7$

Figure 3. and 4. show the SEM-pictures made from coatings, introducing the distinguished layers and EDS sampling areas. Certain layers, phases can be separated very good in the thousand-fold magnification. We have also carried out EDS (Electron Detector System) tests. EDS spectra results are summarized in table 2., a typical measured graphs – zeta phase - can be seen in Figure 5 and 6.
Table 1. the measured micro Vickers hardness values

<table>
<thead>
<tr>
<th>Measuring point</th>
<th>„Technigalva“ sample [HV M]</th>
<th>„Heat treated Technigalva“ sample [HV M]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48,7</td>
<td>98,2</td>
</tr>
<tr>
<td>2</td>
<td>50,7</td>
<td>97,3</td>
</tr>
<tr>
<td>3</td>
<td>45,9</td>
<td>114,2</td>
</tr>
<tr>
<td>4</td>
<td>46,8</td>
<td>92,5</td>
</tr>
<tr>
<td>5</td>
<td>49,7</td>
<td>96,3</td>
</tr>
<tr>
<td>6</td>
<td>45,9</td>
<td>89,5</td>
</tr>
<tr>
<td>7</td>
<td>51,8</td>
<td>101,4</td>
</tr>
<tr>
<td>8</td>
<td>49,7</td>
<td>105,4</td>
</tr>
<tr>
<td>9</td>
<td>45,9</td>
<td>108,2</td>
</tr>
<tr>
<td>10</td>
<td>54,0</td>
<td>112,2</td>
</tr>
<tr>
<td>11</td>
<td>45,9</td>
<td>112,2</td>
</tr>
<tr>
<td>12</td>
<td>42,5</td>
<td>103,5</td>
</tr>
<tr>
<td>13</td>
<td>41,7</td>
<td>96,3</td>
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<tr>
<td>14</td>
<td>43,3</td>
<td>91,2</td>
</tr>
<tr>
<td>15</td>
<td>44,7</td>
<td>91,2</td>
</tr>
</tbody>
</table>

Table 2. EDS spectra result of Fe, Zn and Pb values (%)

<table>
<thead>
<tr>
<th>Layer</th>
<th>Technigalva „T“</th>
<th>Heat treated Technigalva „H“</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe (%)</td>
<td>Zn (%)</td>
</tr>
<tr>
<td>1</td>
<td>16,4</td>
<td>83,6</td>
</tr>
<tr>
<td>2</td>
<td>10,1</td>
<td>89,9</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>21,2</td>
</tr>
</tbody>
</table>

Figure 3. Technigalva layers
○: EDS measuring point

Figure 4. heat treated layers
○: EDS measuring point
2.2. Abrasive tribotester: modified “sand-slurry” equipment

The “sand-slurry” principle is well known in the VI. test category of tribological modeling. Several versions are wide-spread but they agree that for example in a sand with grain composition given - as in abrasive medium – a specimen moves in circular orbit generally with speed given. Great number of specimens can be measured at the same time in abrasive medium given as well as it can be well define but beside in different conditions with the abrasion tester developed in the Institute for Mechanical Engineering Technology. The results got made possible the evaluation according to various standpoints, too.

Figure 7. shows the abrasion tester developed.

The electric motor shaft connects to a worm-gear which gear transmission is 22.58. The working shaft can be found at the exit side of the worm-gear on which 3 pcs. arm cross-clamps can be found – in different heights related to the base plate (Figure 8.) The specimens to be abraded can be fixed in suitable position on this. To one tool, to each arm 3 pcs. altogether 6-6 pcs. specimens can be fixed. Important characteristic of the cross-clamps is that the specimens can be fixed with each other in 90° included position, at their sides in pairs altogether 6 various positions related to the centre of gyration.

The tools are set turned away to one another on the working shaft in top view the circle is divided to 30° sectors. The container containing the abrasive medium can be put into an outer container in case of demand, which can be filled with cooling-heating water to the thermal dynamics of measuring procedure can be regulated.

The abrasive medium was 0/8 OK – type ballast stone. Its average aggregation density in dry condition is 1.7 ton/m³. There is no practically clay-sludge content as it is produced from washed, granulated gravels by knapping. The grain fraction is between 2 and 8 mm.
Figure 7. The “sand-slurry” tester with specimens mounted.

Figure 8. Specimens placed on three levels.

The specimens to be in different radii move with various different peripheral speed in the abrasive medium and the height position results different surface pressure rations (Figure 9). The abrasion tester makes possible exceptional complex evaluation in the function of these variables.
3. RESULTS

3.1. The abrasion and speed connection

We have measured the abrasion of the 6 pcs. heat treated and 6 pcs. not heat treated specimens placed in all three levels (A,B,C) after seven various abrasion time. I have measured the abrasive wear as the decrease of the layer thickness in seven different stage in time, thus getting different sliding distances for each sample in a given time. The surface pressures in standing (not rotating) condition:

\[
\begin{align*}
    p_1 \text{ (A level)} & = 153.83 \text{ Pa} \\
    p_2 \text{ (B level)} & = 521.82 \text{ Pa} \\
    p_3 \text{ (C level)} & = 902.41 \text{ Pa}
\end{align*}
\]

Testing speed range: 14 – 40 m/min

The specimens covered different length with different peripheral speed moving on various radiiuses. After averaging the abrasion results measured at each specimen, repeating three times the measuring series the same incline could be seen at the lines to be adaptable to the plot at heat treated and not heat treated specimens, too. Based on these the speed independence supposed were proved by mathematical – statistical methods, by covariance analyses at all three levels at heat treated and not heat treated specimens, too. The abrasion values of all specimens to be in the different levels can be presented with a single regression straight line. This means that the abrasion values do not depend on the abrasive speed in the speed domain tested (Figure 10. and 11). There is no significant difference between the specimens moved with various speeds but placed at the same level.
Figure 10. Abrasion values of heat treated specimens on “A”, “B” and “C” level (h₁, h₂ and h₃ depth)

Figure 11. Not heat treated specimens abrasion values on “A”, “B” and “C” levels.
3.2. Connection between surface load and abrasion

The specimens placed on the “A”, “B” and “C” level get different surface loads because of this the abrasion values measured on “A”, “B” and “C” levels has to be compared. According to the hypothesis the abrasion values depend on the load. It can be approximated with linear trend-line the appropriate data to different levels on the diagrams, the matching is close in each case. The data appropriate to different levels can be separated visibly however if there is significant difference between them it has to be examined by regression analysis. The worst case is where there is the smallest difference: this is the “A” and “B” level data of the specimens heat treated. The calculations carried out proved that there is significant difference between the abrasion values of specimens fixed on “A” and “B” level. This means that the amount of surface load has significant effect on the abrasion values in the system tested. In case of higher load the specimens have got higher abrasion.

3.3. Comparing the layer structure of coating and abrasion values

During the tests carried out the wear phenomenon occurs in different layers depending on the given stage – sliding distance -. Thus, the wear process reached Eta, Zeta, and Delta phases.

The abrasion measured as a resulting effect on the surface of specimens means the continuous decreasing of coatings with layer structure. In Figure 12. and 13. it can be seen how changes the percentage rate of decisive chemical elements in certain layers of heat treated specimens. The chemical composition’s changing does not influence the abrasion intensity. According to data tested by EDS spectroscopy the percentage rate of chemical elements in the layers of not heat treated specimens is formed otherwise, but this compound does not influence the abrasion intensity of certain layers.
Figure 12. Heat treated specimens abrasion and the connection of layer structure.
Figure 13. Not treated specimens abrasion and layer structure.
4. NEW SCIENTIFIC RESULTS

1. I have verified with statistical methods that the intensity of abrasive wear doesn’t depend on the frictional speed in the model testing system and conditions developed in case of multi-layer hot-dip galvanized coatings. Significant difference couldn’t be demonstrated in the wear intensity of the specimens abraded with different speeds. This statement is valid both to basic and to heat treated coatings in case of different compression conditions, too.

2. I have verified by my measurings that Rabinowicz’s theory is also true in case of multi-layer hot-dip galvanized coatings, where the intensity of abrasive wear depends on the medium pressure and on the resistance of medium deriving from it. There is significant difference in the wear intensity of specimens to be in different pressure levels. The most intensive abrasive wear was found on the place with the highest pressure.

3. The heat treatment improves the abrasion resistance of the multi-layer Technigalva hot-dip galvanized coatings. I have proved with my measurings for the Technigalva coatings that in consequence of heat treatment as a result of thermo-diffusion process the coatings enriches in “Fe” atoms which results significant micro-hardness increase. The higher hardness resulted abrasive resistance increase in case of each speed and of pressure conditions in the testing system.

4. I have proved with SEM exposures and EDS spectroscopy that the heat treatment resulted different layer structures and compositions. I have established that the basis- and heat treated layers have got gradient structures concerning the quantitative occurrence of Zn and Fe – atoms. I plotted the gradient trends based on the results of EDS spectroscopy and I established that the gradient structure of heat treated layers differ substantially from the structure of basis coating. In case of heat treated coating the thickness of certain layers are less different. There are also “Fe” atoms in the two layers are loaded. The “Fe” atom presence to be found in the lower layers of the basic coating doesn’t influence the resultant hardness of the surface.

5. I have established – taking into account the linear abrasion dynamics, the layer decrease speed – that the layer structure of coatings doesn’t appear in the abrasive resistance, the abrasive resistance of certain layers don’t differ. The linear abrasion dynamics of hot-dip galvanized coatings tested was independent.
from the layer – with given composition and hardness – to be in fictional
contact with the abrasive medium.
I have established concerning the abrasive resistance that the resultant effect
comes to full display of the multi-layer coatings having inner gradient structure.
There was no effect of the inner gradient characteristic in the testing system
onto the abrasion intensity measured but the resultant of the different gradient
structure was the different abrasive resistance.

6. I have proved with my measurings that the heat treatment processes are suitable
to modify the resultant abrasive resistance by changing the inner gradient
structure.
5. CONCLUSIONS, SUGGESTIONS

Nowadays it is already a demand for the users to develop abrasive – and friction resistant coatings beside corrosion resistance at hot-dip galvanized surfaces exposed to abrasion. It is clear from studying the technical literature that the abrasive conditions of coatings with different layer composition is not made clear so far by the research works. The aim of my research work helping the practical utilization is to determine with rapid, reproducible laboratory tests that the different coatings what abrasive resistance have got in connection with each other. Furthermore to determine the possible connections between the abrasive resistance and layer structure, to give connections between the abrasion, the length covered, the speed and the pressure of abrasive medium.

According to the VI. testing category of the DIN 50322 standard the Technigalva® hot-dip galvanized coating and its heat treated modified version - Technigalva® H – were tested. Based on the tests carried out I have disclosed connections in the validity range of the testing system:

- Between the abrasion and abrasive speed, which made more accurate new abrasion dynamics knowledges.
- Between the abrasion and surface load, which means extending the former Rabinowicz theory.
- Between the abrasion and surface hardness, which made more accurate the role of surface hardness of metals concerning abrasion.
- Between the abrasion and layer structure of coatings, which threw upon light to the decisive role of the resultant abrasive resistance of the gradient structure materials.

I have verified with my measurings that the heat treatment processes are suitable to modify the resultant abrasive resistance by changing the inner gradient structure. With researching the parameters of heat treatment technologies to achieve the ideal abrasive resistance, changing the layer structure and its characteristics is an effectual means for further layer development research works.
6. SUMMARY

During my research work I have studied the abrasion resistance a newly arisen load of the multilayer hot-dip galvanized coatings.

The hot-dip galvanizing is a technology used to protect the surfaces of iron- and steel constructions, of piece goods against permanent corrosion, which protective effect depends mainly on the thickness of surface layer and on its density. Its main application fields suggested are the atmospheric load in every corrosion class as well as the surface protection of metal constructions of ventilated insides. Its application spreads continuously because of the reliable protective effect of the coating, the industrial scale applicability of the process, comparatively high productivity and because of small labour requirement.

Mechanical loads also affect the products beside corrosive affects at industrial, agricultural and public place pavement grids at industrial filters hot-dip galvanized spreading nowadays. It is already a utilizing demand nowadays to develop an abrasion and rubbing resistance coatings at surfaces hot-dip galvanized exposed to abrasion, to sand - and breakstone scatter. There are not at disposal neither in technical literature nor in database of coat-producing and of developing companies comparative regulated measuring data concerning abrasion resistance. These data are indispensable to develop technology improving the abrasion resistance.

The aim of my research work was to determine with rapid comparative laboratory abrasion tests that the coatings with different composition hot-dip galvanized what abrasion resistance got as compared to with each other. Within the scope of this:

- the aim is to produce such measuring results which represent with properly scientific test basis the differences between abrasion resistance of hot-dip galvanized coatings with different compositions
- to give empirical characteristics in the function of frictional length, of speed and of abrasion medium pressure for developing technology improving abrasion resistance.

Based on the producer’s recommendations the Technigalva® and its modified variation by heat treatment - Technigalva® H-coatings were tested. Before abrasion test I have determined the specimens hardness values in case of natural and heat treated coatings alike.

I made metallographic specimen and microscopic exposures determining the characteristic layer structure.

I have carried out EDS spectrometric measurings for following track of the changes of material composition and SEM exposures for detailed structural analysis respectively.

I have planned and manufactured a model testing system for the abrasion tests of specimens coated simulating the loading and frictional properties and the temperature conditions of pavement grids applied in agriculture.
I planned the laboratory abrasion tester to be suitable to the criterion of the VI. testing category put down in DIN50322 standard namely it should be suitable for comparative tests with simple specimens in reproducible measuring system. I have guaranteed by suitable developing the “sand-slurry” abrasion tester that during one measuring process two specimen types (different coatings) should be able to be compared at three different load levels, at six different frictional speeds. Classified, washed ballast-stone was used as testing medium. I solved the abrasive wear of coatings by measuring the layer thickness to which I applied a gauge with eddy (Foucault) current surface feeler.

Based on the tests carried out I have established connection in case of natural and heat treated Technigalva hot-dip galvanized coatings:
- between the abrasive wear and abrasive speed,
- between the abrasive wear and surface load,
- between the abrasive wear and surface hardness,
- between the abrasive wear and layer structure of coatings.

The results of the research work guarantee further significant help for further developing hot-dip galvanized coatings, for further research of heat treatment processes, for the introducing to the market of products with more reliable and longer service-life.
7. PUBLICATIONS IN CONNECTION WITH THE THEME OF DOCTORAL DISSERTATION

Articles in foreign language:


Articles in Hungarian language:


