INFLUENCE OF MICROSTRUCTURE ON QUALITY OF PHOSPHATE FILMS

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Abstract

Target of this work was to compare the phosphate films properties, which were applied on screws with various surface conditions after heat treatment respectively chemical heat treatment – specifically enriched (sample 1), enriched by decarburize surface (sample 2) and enriched by carburize surface (sample 3). The properties control was realize by light microscopy – measurement of films thickness (Table 1) and scanning electron microscopy – evaluation of morphology of phosphate crystals. There were used screws as an experimental material produced from WNr. 1.7034 material with strength about 1120 – 1200 MPa. The morphology of phosphate film was evaluated on REM by SE regime. Phosphate crystals by sample 1 and 2 have acicular profile; sample 3 has imperfect acicular profile with local amorphous formations. From theoretical analysis of obtained experimental data result that phosphate films are perfectly segregate on non-affected metallic surfaces. The smallest thicknesses were measured by carburize screw. Probably it is a result of increased carbon concentration follow the most carbide quantity which allocates generally higher chemical resistance against phosphate bath and inhibited to entry of phosphate solution on surface. This fact is proving by speed deceleration of phosphate process. There was observed the surface oxidation by decarburize sample. Created oxides (Fe₂O₃) influence as a barrier and therefore the phosphate bath contains phosphoric acid, this leads to oxides disposal in process of phosphating. Consequently is shortening of the real phosphating time and film irregularity. The surface morphologies shown that finish phases of phosphate crystal segregation working by analogical mechanism.

1. INTRODUCTION

In spite of rich knowledge of corrosion process the corrosion affected the huge economical losses in the world. There is around 4 to 5 % of GDP in advanced industrialized countries. The aim of anti-corrosive protection is minimalism the corrosion speed by occurring the high period of service and safety of metal parts. Into the processes of the surface treatment belong such modes of chemical or electrochemical metallic treatment where is created inorganic non-metal film on the metal surface. If this film is created by reaction of metal surface with environment in presence of the metal we can say about a protective conversion films. Phosphatizing is chemical process of metal surface treatment where is created the crystalline film of insoluble zinc phosphate, Ca - Zn, Fe and Mn. Created film which is chemically wired in basic metal is porous and especially used for application of substance undercoat following increasing the anchorage adhesive surface respectively as an anti-corrosive protection. Important factor which influence on quality of phosphate film is the surface condition of backing part.

The aim of this work is to compare the phosphate films properties, which were applied on screws with various surface conditions after heat treatment respectively chemical heat treatment.
2. EXPERIMENTAL MATERIAL

Primary screw marked as M12x205, figure 1, are applied for automotive field and are made from material WNr. 1.7034, where the chemical composition is presented in Table 1 and comply approximately with STN 41 4140. There are refinements on strength of 1120 to 1200 MPa with sorbite structure after heat treatment. By operation of phosphatizing was devoted the big regard on preparation of surface because each contamination lead to precluding or difficult realization in reactions process by surface treatment. In process of phosphatizing was used the zinc – calcium phosphate which consists from zinc nitrate, calcium nitrate, dihydrozincphosphate and orthophosphoric acid.

<table>
<thead>
<tr>
<th>Chemical element</th>
<th>Min %</th>
<th>Max %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0,34</td>
<td>0,41</td>
</tr>
<tr>
<td>Si</td>
<td>0,40</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0,6</td>
<td>0,90</td>
</tr>
<tr>
<td>P</td>
<td></td>
<td>0,035</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td>0,035</td>
</tr>
<tr>
<td>Cr</td>
<td>0,9</td>
<td>1,2</td>
</tr>
</tbody>
</table>

Fig. 1 Screw M12 x 205

In process of heat treatment can occur the situation when reach to aberration and surface of part is recarburized or decarburized. From mentioned reason were same screws laboratory recarburized and decarburized.

3. EXPERIMENTAL RESULTS

3.1 Estimation of thickness of phosphate films

Thickness of surface films influences on property than chemical rezistivity and is the ground of next exams. By consecutive evaluation of quality of surface treatment belongs the film thickness to baseline straight indicators the expected efficiency of realized protection against corrosive influence of environs. Thickness is straight influenced the barrier effect of film, its compactibility, porosity and many physical – mechanical properties. Film thicknesses were estimated by metallographic method on the cross-section according to STN 42 0449 by light microscope JENAVERT.

In terms of estimated aims were chosen 3 screws with following identification:

Sample 1 – real condition
Sample 2 – decarburize screw
Sample 3 – cemented screw.
Table 2 Minimal and maximal thickness of phosphate film and the average thicknesses of particular samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Minimal – maximal thickness [μm]</th>
<th>Average thickness [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6 – 16</td>
<td>9,8</td>
</tr>
<tr>
<td>2</td>
<td>2 – 10</td>
<td>6,6</td>
</tr>
<tr>
<td>3</td>
<td>2 – 8</td>
<td>4,6</td>
</tr>
</tbody>
</table>

The film in case of sample 1 and 2 were evaluated as continual and unstable, film in case of sample 3 was interpreted as incoherent and unstable.

3.2 Microstructure
The evaluation of microstructure and depth of recarburizing respectively decarburizing was realized on samples above. Microstructure of the core of sample 1 is illustrated on figure 5 and created mostly by bainite. The changes as recarburizing, decarburizing and respectively another influence of surface area weren’t occurred. Microstructure of core for sample 2 is pearlitic – ferrite and the structure respond to state after normalizing, figure 6. Subsurface layer is to the depth of 0, 06 mm completely decarburized and the microstructure is created of almost pure ferrite, figure 8. Figure 8 together illustrated the oxidation of grain boundary to the deep cca 0, 02 mm. In direction of surface to the core part the rate of pearlite is rising, in dimension of 0,2 mm to the surface grinding into the microstructure of core. The microstructure of core for sample 3 is created by fine and low tempered martensite, figure 7. The estimated depth (according of STN 42 0449) of decarburized layer is approximately 1,1 mm and documented on figure 9. Nearly by core is created by acicular low tempered martensite and residual austenite, figure 10.
3.3 The evaluation of morphology of phosphate film on REM

Morphology of phosphate film was evaluated on REM TESLA BS 340 a is documented on figures 11, 12 a 13.

From presented photo documentation is possibly to allege, that the phosphate film of sample 1 is created by acicular crystals of standard form, where sample 2 has the acicular character most expressive. In case of sample 3 is the segregated phosphate in form of crystals of imperfect acicular form with observation of amorphous formations.
3.4 Results analysis and summary

The measured average thickness of phosphate film was miscellaneous by each sample. Real sample has value of 9.8 μm; the recarburized sample has thickness of 6.6 μm and value by recarburized sample is 4.6 μm. The thickness differences of phosphate films are explained by several surface conditions before the process of phosphatizing.

From the theoretical analysis of experimental results and practical experiences accrues that the best segregate phosphate film is on surfaces of pure metals. The biggest thickness of phosphate film was in case of real screws. But the smallest thickness was noted by cemented sample. Most likely is the result of enhanced carbon concentration in following presence of more carbide’s which have bigger chemical resistance towards phosphate bath. At the same time there inhibit to approach of phosphate solution on the surface which is prove by reducing of phosphatizing process. In case of decarburized sample also automatically run the oxidization on sample surface during the process of heat treatment. Oxidizing layer contains many types of oxides where on the most upside are the stable oxide of Fe₂O₃ the affected as a barrier during phosphatizing. Considering phosphating bath contains the phosphoric acid there reach to oxides disposal in process of phosphatizing and the overall result is shortening of the real time of phosphatizing and unstable film.

In case of sample 3 were observed amorphous formation, the in case of other samples was the phosphate segregated in form of needles. From mentioned we can allege that the final phases of crystal segregation of phosphate were running by analogical mechanism.

From these results accrue that each affection of parts surface before phosphatizing influence on thickness, uniformity and integrity of segregated films. Hence is important to control the quality of delivered parts before its surface treatments for prevention of reclamation or part devaluation.

LITERATURE