EFFECT OF CORROSION ON THE MECHANICAL PROPERTIES OF MAGNESIUM ALLOY AZ91

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Keywords: magnesium alloy, corrosion, microhardness

1. Introduction

Magnesium alloys are characterized by excellent mechanical properties in comparison with low density. These properties are nowadays mainly used in the automotive and aerospace industry. The reason is construction relief and thereby reduced fuel consumption, leading to the reduced financial costs and environmental protection.

On the contrary to excellent mechanical properties the negative aspect is low corrosion resistance of magnesium alloys. This is the reason why the magnesium alloys are not used more often.

The various phases present in magnesium alloys are characterized by different electrochemical potential and different mechanical properties. Complicated phase structure of the magnesium alloy influences both corrosion processes, and interaction passivating agents with magnesium alloy.

2. Experimental

2.1. Sample preparation

Magnesium alloy AZ91 was studied. Its chemical composition (wt.%) was 8.90 Al; 0.68 Zn; 0.20 Mn and the balance was Mg. Samples were polished with 600 grit SiC paper and degreased by STAR PN 75 in ultrasonic bath for 2 minutes. Than the samples were rinsed by distilled water and ethanol and dried by hot air.

2.2. Immersion test

The samples were hung on insulated wire and they were immersed into corrosion environment. Corrosion environments were distilled water and sodium chloride solution (3%). Durations were 1, 8, 48 and 168 hours, respectively.

The corrosion products were removed in suspension of 5 g silver chromate (Ag2Cr2O7) in 15% aqueous solution of chromium trioxide (CrO3). Temperature of the bath was 90–100 °C. Then the sample was rinsed by distilled water and by ethanol and dried by hot air.

2.3. Metallography

Corroded part of the samples were cut out by handsaw and mounted in resin. The samples were polished with 1200 grit SiC paper, then with 1 µm diamond paste. Polished samples were etched (0.4 g picric acid; 0.7 cm³ distilled water; 0.3 cm³ acetic acid and 40 m³ ethanol) and observed by microscope Neophot 21 (Zeiss Jena).

2.4. Vickers microhardness tests

Microhardness was studied with LECO LM247 AT with a square-based pyramid diamond.

The samples were polished with 1200 grit SiC paper. The microhardness was measured at nine points of cross sections of the samples. Tests were repeated several times. Distances between indentations were 250–300 µm.

3. Results

Magnesium alloy AZ91 corroded in distilled water and in sodium chloride solution (3%).

The corrosion damage in distilled water reached through all profile of the samples (Fig. 1) and affected microhardness (Fig. 3). Higher values correspond to α-Mg and lower values are caused by corrosion. Microhardness was measured twelve times because of large spread of values in this case (Table I).

Corrosion in sodium chloride solution (3%) took place by typical pitting mechanism (Fig. 2). The corrosion damage was situated on the surface. The value of microhardness (Fig. 3) at each point differs for α-Mg (lower values) or intermetallic phase Mg17Al12 (higher values). In comparison with sample corroded in distilled water (Fig. 3), this sample had different mechanical properties.

Microhardness of pure AZ91 can be compared to microhardness of magnesium alloy AZ91 corroded in sodium chloride solution (3%).

Table I

<table>
<thead>
<tr>
<th></th>
<th>Microhardness (HV 0.3) of uncorroded AZ91 and corroded (48 hours) by distilled water and NaCl solution (3%)</th>
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<tbody>
<tr>
<td>Uncorroded</td>
<td>67.3</td>
</tr>
<tr>
<td>Distilled water</td>
<td>60.5</td>
</tr>
<tr>
<td>3% NaCl</td>
<td>59.5</td>
</tr>
</tbody>
</table>

s854
4. Conclusions

Corrosion of magnesium alloy AZ91 in distilled water affected mechanical properties (microhardness) more in comparison to corrosion in sodium chloride solution (3%).

Corrosion in distilled water passed through all the profile of the samples. Because of that the microhardness was affected in all profile of the sample. On the other hand, corrosion in sodium chloride solution (3%) affected only surface of the sample AZ91.

Studied alloy AZ91 was processed by gravity casting, during cooling probably rose intergranular stresses that made these regions more reactive. Then in distilled water, crevice corrosion with hydrogen depolarization (at relatively low value of pH) was more pronounced. It can be stated, that there was a large spread of values of the sample corroded in distilled water corresponding to heterogeneity of corroded material.

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REFERENCES


J. Tkacz, M. Zmrzlý, and J. Wasserbauer (Brno University of Technology, Faculty of Chemistry – Centre for Materials Research, Brno, Czech Republic): Effect of Corrosion on the Mechanical Properties of Magnesium Alloy AZ91

Corrosion properties of magnesium alloy AZ91 were studied in distilled water and sodium chloride solution (3%). Corrosion resistance of Mg₁₇Al₁₂ phase was better than corrosion resistance of other Mg-phases. Microhardness profile was evaluated across the sample to show negative impact of the corrosion on the mechanical properties of magnesium alloy AZ91.
THE EFFECT OF DUPLEX COATING ON WEAR PROPERTIES OF TOOL STEELS

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Keywords: Duplex Coating, Nanohardness, Tribological Properties, PVD

1. Introduction

This paper develops in more detail results listed in paper Characteristic of Duplex Coated Steels1. The requirements for materials used in the machine parts production, especially their functional characteristics and service life are currently increasing. Thin ceramic coatings deposited on the surface of tools and machine parts by PVD methods improve considerably their tribological properties. These hard brittle coatings can be damaged rapidly if a plastic deformation initiates in the substrate near the coating-substrate interface when subjected to relatively high intensity loading. Therefore, the strengthening of substrate surface layers, e.g. by plasma nitriding, appears to be a suitable solution for the low strength of the substrate2.

2. Experimental procedure

The specimens from low-alloy steel 31CrMoV9 were austenitized, inert gas quenched and tempered. The duplex treatment proceeded in two phases. In the first phase the specimens were pulse plasma nitrided (further PN). In second phase different PVD coatings were deposited – a) TiN (thickness 1 and 3 μm), b) CrN (thickness 1 and 3 μm), c) TiAlN (thickness 3 μm) and d) multilayer 3×(TiN-CrN) (thickness 3 μm).

Nanohardness and elastic modulus of the coatings were measured. Evaluation of nanohardness was made by CSM method with maximum load \( P_{\text{max}} = 670 \text{ mN} \). The measurement methodologies is described in ref.3 and ref.4. The specimens were tested on tribometer „pin-on-disc“. The experiments were realized at the temperature 22 °C and 350 °C, with load 1, 2 and 5 N, all under conditions of dry friction. Wear marks profiles were measured with profilograph Talysurf 6.

3. Results and discussion

The results of nanohardness and elastic modulus are shown in Table I. The results of wear marks measurement are shown in Table II. Records of wear marks’ measurement on profilograph are shown at Fig. 1.

Table I

<table>
<thead>
<tr>
<th>Coating</th>
<th>Hardness [GPa]</th>
<th>E [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PN + TiN</td>
<td>35,8 ± 4,6</td>
<td>504 ± 80</td>
</tr>
<tr>
<td>PN + CrN</td>
<td>26,9 ± 3,4</td>
<td>327 ± 43</td>
</tr>
<tr>
<td>PN + TiAlN</td>
<td>32,9 ± 5,8</td>
<td>497 ± 98</td>
</tr>
<tr>
<td>PN + 3x(TiN-CrN)</td>
<td>34,2 ± 8,1</td>
<td>566 ± 83</td>
</tr>
</tbody>
</table>

Table II

<table>
<thead>
<tr>
<th>Testing temperature</th>
<th>22 °C</th>
<th>350 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load</td>
<td>1 N</td>
<td>2 N</td>
</tr>
<tr>
<td>Coating PN + CrN</td>
<td>1,36</td>
<td>1,44</td>
</tr>
<tr>
<td>Coating PN + TiN</td>
<td>1,8</td>
<td>2,48</td>
</tr>
<tr>
<td>Coating PN + TiAlN</td>
<td>2,2</td>
<td>2,44</td>
</tr>
<tr>
<td>Co. PN+3×(TiN-CrN)</td>
<td>2,3</td>
<td>2,48</td>
</tr>
<tr>
<td>Parent material(PM)</td>
<td>0,72</td>
<td>1,2</td>
</tr>
</tbody>
</table>

Fig. 1. The record of measurement on profilograph Talysurf 6 for particular coatings after testing on tribometer Pin-on-Disc at temperature 350 °C.
Fig. 1 shows the change of surface roughness $R_z$ with deposited PVD coating compared with only nitrided sample. The only nitrided sample, PM, has markedly lower roughness than all PVD coated specimens, though all specimens had the same roughness before PN. Reason is creation of clusters, which are created using PVD treatment by arc.

At Table III the wear of ball (countepart) after “pin on disc” test is shown. At temperature 22 °C and load 1 N maximum wear was reached with TiAlN coating. Under load 5 N the wear is for all coatings similar. Only nitrided PM had the wear of the ball much lower. Results of friction during pin on disc measurement are shown at Fig. 2 and 3. The lowest friction coefficient had CrN coating. The friction coefficient of PM, at 22 °C, increased with friction distance because of adhesion.

**Table III**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>20 °C</th>
<th>250 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PN + TiN</td>
<td>514</td>
<td>586</td>
</tr>
<tr>
<td>PN + CrN</td>
<td>535</td>
<td>592</td>
</tr>
<tr>
<td>PN + TiAlN</td>
<td>850</td>
<td>653</td>
</tr>
<tr>
<td>PN + 3x(CrN-TiN)</td>
<td>450</td>
<td>592</td>
</tr>
<tr>
<td>PM</td>
<td>90</td>
<td>505</td>
</tr>
</tbody>
</table>


![Fig. 2. Graph of friction coefficient and distance, load 5 N and temperature 22 °C](image)

Fig. 2. Graph of friction coefficient and distance, load 5 N and temperature 22 °C

![Fig. 3. Graph of friction coefficient and distance, load 5 N and temperature 350 °C](image)

Fig. 3. Graph of friction coefficient and distance, load 5 N and temperature 350 °C

Experimental results show that the friction coefficients of the samples with duplex coatings firstly increases and consequently settles during testing. The mechanism of deterioration of the duplex coated steel is a combination of adhesive and abrasive wear. The adhesive wear took place on the disk during experiment while the ball was worn down in an abrasive manner. The evidence of abrasive wear can be seen on the grooves formed on the ball during experiment.

### 4. Conclusion

The conclusions drawn from the experiment show that duplex treatment is a useful way to increase the die service life and that the most suitable coating is the TiN coating. This coating in combination with a nitrided substrate had a low friction coefficient and a small wear.

As far as the coating hardness is concerned, the most favourable is the coating CrN and multilayer coating 3x(TiN-CrN), because it has the gentle increase of microhardness in depth profile. The max hardness is higher for TiN and TiAlN coatings, so there is steeper change of hardness between nitrided layer and PVD layer, causing risk of the coating cracking, but it did not occur in our measurement. So these coatings exhibit better service life and friction coefficient.

Current thin abrasion-resistant surface layers and duplex coatings bring remarkable extension of service life and reliability to parts, tools and dies as confirmed by this research. Still most technologies have not managed to reach the limits of their possibilities so far.

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### REFERENCES


M. Válová and J. Suchánek (CTU in Prague, Prague, Czech Republic): The Effect of Duplex Coating on Wear Properties of Tool Steels

The paper resumes partial results of tribological testing of duplex coatings of tool steel. Steel samples (31CrMoV9) were nitrided and subsequently treated by PVD process. There were deposited different coatings (TiN, CrN, TiAlN and multilayer 3x(CrN-TiN)) with 1 μm and 3 μm thickness. Samples were tested and their nanohardness, hardness of duplex coating, coefficient of friction, coating thickness (calotest), resistance against adhesive wear (scratch test) and abrasion size (HEF) were measured. Results of friction coefficient measured by “pin on disc” tribometer and wear marks measured by contact profilometry were are summarized.
PROPERTIES OF RENOVATION LAYERS APPLIED BY SUBMERGED ARC WELDING

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Keywords: wear, repairing, cladding, submerged arc welding-on (SAW), microhardness

1. Introduction

Continuous steel casting lines are one of the key facilities in steel processing. Steel mill rolls play a vital part in the production of steel products. Lifespan of rolls, which provide movement of slabs along the line, is very important for ensuring their reliable operation. During steel production, rolls are loaded with the combination of wear with thermal fatigue caused by thermal shocks when moving slabs in the temperature range 1280 °C to 850 °C and also with high-temperature corrosion. The combination of these stresses causes rapid wear on the surface of new rolls. Currently, the renovation of continuous steel casting rolls used to be carried out by submerged arc welding (SAW). Worn roll layers deposited on the roll surface. The first layer deposited on the base material was the interlayer, welding wire UP5-GF-45-C DIN 8555 in combination with aluminous – basic flux provided by welding wire producer is 450 HV. Welding position used according to STN EN ISO 6947-PA. This position is most suitable for repairing of rotary surfaces and by using a flux it is usable without other technology modifications of welding machine. There were three cladding layers deposited on the roll surface. The first layer deposited on the base material was the interlayer, welding wire UP5-GF-200-C DIN 8555 in combination with aluminous – basic flux S F AB 1 65 AC H5 EN 760 was used. Cladding hardness provided by welding wire producer is 190 HV. Flux was dried 1 hour at 300 °C before cladding. Properties of flux used are as follows: basicity index 1.3, flux granularity 0.2–2.0, density 1.2 kg dm−3, suitable for AC and also DC welding current supply, hydrogen content ≤ 5 HDM.

Next there were two cover layers deposited using welding wire UP5-GF-45-C DIN 8555 and the same aluminous – basic flux as in previous S F AB 1 65 AC H5 EN 760 by SAW technology on interlayer. Cover cladding hardness provided by welding wire producer is 450 HV. Welding parameters are given in Table I. Roll preheating temperature: 260–270 °C. During welding process the interpass temperature was kept up with the help of gas-burners at 200–380 °C. After cladding the roll was treated by stress revealing at 520 ± 10 °C, held there for 4–5 hours and finally cooled slowly (cooling rate 40 °C per hour) to the temperature of 210 °C in isothermal wrap. When the roll temperature was 210 °C, next cooling continued in the air. According to STN EN 25 817 required quality rank was „B“. Cladding quality was evaluated by visual test according to STN EN 970 together with the capillary test according to STN EN 1289 and ultrasonic detection according to STN EN 1712.

Metallographic analysis was carried out according to STN EN 1321 on cross sections of particular cladding layers. Abrasive wear of repaired rolls was compared with the reference material of new roll with surface hardened layer thickness 4mm. Abrasive wear test based on weight analysis was performed on a laboratory device APGi, VEB Leipzig. Two corundum abrasive papers with different granularity marked as P 200 and P 800 were used. Surface exposed to abrasive wear was functional roll surface – cover cladding layer.

2. Materials and methods

Experimental works were aimed on the evaluation of rolls repaired by submerged arc welding (SAW). Worn roll comes from curved sector of continual steel casting line and was made of material 41CrMo4 EN 10083-1-91 by forging.

Welding position used according to STN EN ISO 6947-PA. This position is most suitable for repairing of rotary surfaces and by using a flux it is usable without other technology modifications of welding machine. There were three cladding layers deposited on the roll surface. The first layer deposited on the base material was the interlayer, welding wire UP5-GF-200-C DIN 8555 in combination with aluminous – basic flux S F AB 1 65 AC H5 EN 760 was used. Cladding hardness provided by welding wire producer is 190 HV. Flux was dried 1 hour at 300 °C before cladding. Properties of flux used are as follows: basicity index 1.3, flux granularity 0.2–2.0, density 1.2 kg dm−3, suitable for AC and also DC welding current supply, hydrogen content ≤ 5 HDM.

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Metallographic analysis was carried out according to STN EN ISO 1321 on cross sections of particular cladding layers.

3. Results

Fig. 1a shows microstructure of roll base material – fine-grained martensite. Fig. 1b shows influence of heat introduced by welding on martensitic microstructure. The heat caused change of grain size and highlighting of grain boundaries. The increased occurrence of inclusions and precipitates on grain boundaries was observed. Transition from the base material to HAZ (heat affected zone) is continuous. This region can be designated as critical. Interlayer, Fig. 1c, has structure with characteristic epitaxial grain growth. Structure of interlayer is martensite-ferrite, also called semi-ferritic structure. Structure of cover layer, Fig. 1d, is martensite-ferrite. Thickness of cover layers after cutting operations to required dimension varied in the range of 3.0–3.5 mm.

Maximum microhardness value 410 HV0.01 was found in cover layer in 1mm distance from the surface. The lowest hardness values (from 239 HV0.01 to 243 HV0.01) were found in base material. Interlayer hardness is affected by cladding metal shuffle with cover layer metal, Table II.

Table I Parameters of roll cladding

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<tbody>
<tr>
<td>1</td>
<td>3,2</td>
<td>480–500</td>
<td>30–32</td>
<td>45</td>
<td>31</td>
<td>35</td>
<td></td>
<td></td>
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<tr>
<td>2</td>
<td>2,8</td>
<td>360–400</td>
<td>28–29</td>
<td>45</td>
<td>29</td>
<td>34</td>
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</tbody>
</table>

*Corresponding author
Larger abrasive effect on the sample with claddings showed corundum abrasive paper P 200, Fig. 2. Lower abrasive effect was observed for corundum abrasive paper P 800. The measured values of weight losses are consistent with the hardness of the contact surfaces of samples exposed to abrasive wear.

4. Conclusion

Metallographic analysis identified structure of the base material and particular cladding layers. The highest average hardness was measured in the cover layer at a distance of 1 mm from the surface, 410 HV0.01. The lowest hardness is shown by the base material, 239–243 HV0.01.

New hardened cylinder showed higher abrasive wear resistance in comparison with renovating layers.

Rolls will wear differently from machine to machine and within machines. When choosing a surfacing alloy, a balance between each wear factor with the focus on the primary wear factor, should be considered.

This work was done within the scientific project VEGA No. 1/0510/10.

REFERENCES


J. Viňaš, J. Brezinová, A. Guzanová, and D. Lorincová (Technical university of Košice, Faculty of Mechanical Engineering, Department of Technology and Materials, Slovakia): Properties of Renovation Layers Applied by Submerged Arc Welding

The paper presents an analysis of the quality of cladding layers deposited on continuous steel casting rollers made of material 41CrMo4 EN 10083-1-91 using destructive methods. The research works were aimed on the effect of chosen welding wire on the tribological properties of claddings. There was also monitored mixing of cladding metal with the base material at welding parameters used together with the effect of heat input in the process of cladding. Weldability and influence of the chemical composition of welding wires on resulting properties of cladding were also evaluated. There are presented proceedings that are necessary to be taken into account at rollers renovation process, and also the development of research in the studied area.