Development of a plasma surface treatment for magnesium alloys to ensure sufficient wear and corrosion resistance

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Abstract

Extensive investigations of the authors showed the possibility of producing reliable plasma vapour deposition (PVD) hard coatings on magnesium alloys with good wear properties comparable to PVD coated steel or titanium based alloys. In presence of corrosive mediums crucial contact and pitting corrosion, induced by process related coating pinholes are the main failure mechanisms of coated magnesium alloys, even without any tribological load applied. The authors developed the new method of plasma anodisation to ensure acceptable corrosion resistance. In contrast to conventional anodisation processes the aqueous electrolyte is substituted by an oxygen plasma. The main advantages are that the process uses no toxic electrolytes, there is no waste and anodising and PVD-coating can be done in one process. The article gives a brief view of our extensive work starting from the first approach in PVD deposition of magnesium alloys up to the present work in establishing the plasma anodisation.

Keywords: Plasma anodisation; Magnesium; Corrosion; Wear; PVD; Al₂O₃

1. Introduction

The care for brief resources and the economical use of primary energies are one of the great political and technological challenges of this new century in order to lower emissions and to reduce the increasing environmental pollution. Concerning this background magnesium seems to be very prospective to fulfil these demands. Besides its high strength/weight ratio, magnesium alloys connect the demands of good machinability and a great recycling potential.

Magnesium alloys provide promising alternatives to aluminium alloys for the manufacture of cast automotive components and there has been increased research and use in automobile production during the last few years.

Because of their high strength/weight ratio magnesium alloys are very prospective materials for application in the moved component field. However, their low corrosion resistance, low capacity for strengthening, poor ductility and especially their unsatisfactory wear-behaviour result in until yet the use of magnesium alloys is restricted to static components.

Because PVD hard coatings with a few micrometres thickness have been successfully developed since years for different tribological applications it is thought that the wear behaviour of magnesium alloys can strongly be improved by suitable, reliable PVD coatings.

2. Results

The approach of the authors to ensure sufficient wear and corrosion resistance is to develop suitable, reliable PVD coatings on magnesium alloys. It was made use of the experience of the authors in PVD deposition technique by using deposition parameters for the magnesium coating, which produce reliable coating qualities on conventional materials [1]. Because of its superior properties CrN was chosen as coating material. For all investigations the magnesium die cast alloy AZ91D was used.

The characterisation of the coating–substrate compound showed minor coating adhesion than on steel and practically no formation of compressive residual stresses in the coating, which influence adhesion and hardness (Table 1).

Due to their low reduction potentials light metal alloys like magnesium and aluminium are susceptible to the
formation of surface oxidation films even after short exposure to atmosphere. While on the aluminium a dense and self passivating oxide film is formed, the oxidation film on the magnesium is fragile and unstable. This fragile oxide film is a result of a misfit between the lattices of the cubic oxide and the hexagonal metal concerning the pilling-bedworth factor -1. This oxide film reacts in presence of humidity to form hydroxide, which is believed to decrease adhesion and formation of compressive residual stresses due to the formation of shear planes in the coating–substrate interface. This assumption is supported by the fact that SIMS depth profiles showed an enrichment of oxygen in the magnesium AZ91–CrN coating interface.

In order to remove the surface oxide film the focus of attention was turned towards the sputter etching process of the magnesium surface as deposition pretreatment. Therefore, 30 Å thick Cr-films were deposited on AZ91 by variation of the sputter etching parameters Table 2. Afterwards the interface between coating and magnesium was analysed with XPS depth profiles. Fig. 1 shows the depth profiles of the O binding energy with and without sputter etching. Considering a sputter rate of 1 Å/min the interface is reached after 30 min of XPS-sputtering. Without sputter etching low oxygen content is detected in the interface.

Besides the removing of the oxide film and as a result of this a better coating adhesion and the lasting formation of residual coating stresses, the coating hardness is also increased by the sputter etching. The etching does not only remove the thermal oxide film but also produces a kind of nano-surface roughness, which also influences adhesion in a positive way, and a refinement of the coating grain structure. A detailed review of the sputter etching process of magnesium AZ91 is given by Hoche et al. in [5].

After successful optimization of the CrN coatings, wear tests were carried out using an Optimol SVR III high temperature tribometer. The tests were carried out in unlubricated oscillating motion against a 100Cr6 counterbody. The extensive investigations included the variation of load and temperature in order to obtain the parameter field where CrN coated AZ91 can be put into service [6]. Fig. 2 shows the results of CrN coated AZ91 in comparison to other CrN coated base materials (100Cr6, TiAl6V4, S 6-5-2, AlMgSi0.5) tested with similar parameters [7].

From the test results there is no doubt that in a certain parameter field CrN coated AZ91 can be put into service. Nevertheless, because of its unsatisfying load
carrying capability the applied area pressure for magnesium alloys is strongly limited. Otherwise compound deformation, coating cracking and coating detachment can occur-like as it is shown in Fig. 2c.

A dependence existing between the values load and temperature in a way that if one of the parameters temperature or load is increased, the maximum value of the competitively parameter at which the system can withstand the tribological load conditions is lowered. A detailed review of the wear results is given by the authors in [6].

Information about the corrosion properties was obtained in the salt spray test according DIN 50021 SS. Fig. 3a shows an overall view of the corrosion attack of a 9 \( \mu \)m thick CrN coating on AZ91. The surface was analysed with SEM and profilometry. There is crucial corrosion attack with craters with depth more than 1 mm. As can be seen from the profilometry the surface attack is non-uniform.

The process related pinholes are assumed to lead to crucial contact corrosion attacks, which act as localised electrochemical corrosion elements leading to the dissolution of the magnesium substrate. While the pinholes do not influence the wear properties in a negative way, their effects on the corrosion properties are fatal. In particular metallic or metalloid coatings with a more positive potential than magnesium take over the function of the cathode, which leads to a high current density of the anode, that is the base material at the pinholes, and results in a rapid anodic dissolution of the magnesium.

As a consequence of this a suitable surface pretreatment before the PVD deposition is needed in order to ensure sufficient corrosion protection. A number of commercial surface treatments for the corrosion protection of magnesium are well established, which are mainly based on anodising and chromating. These methods use aqueous electrolytes and are subjected to severe legal restrictions due to the use of harmful materials and the high amount of toxic waste. Furthermore, the process related high roughness of these surface treatments complicates the subsequent PVD deposition or even makes it impossible.

Therefore, our requirements for a suitable surface treatment are:

- Environment friendly (no aqueous and/or toxic waste).
- Implemented in the PVD-process to allow an immediately post-deposition.
- No increasing of surface roughness to ensure PVD-coating.

A promising method which fulfils our requirements and which seems prospective to produce surfaces for tribological-corrosive complex demands in one process is assumed by the plasma anodising of magnesium and the subsequent PVD hard coating deposition. Already, in the 1960s plasma anodisation of magnesium was mentioned in literature [8–10]. The process is comparable with the anodisation in aqueous electrolytes, substituting the aqueous electrolyte with oxygen plasma. At the anodised magnesium substrates a positive BIAS voltage is applied. Both processes can be done in a commercial sputter unit. A detailed description of the extensive work of the authors in developing a suitable anodising procedure can be found in [11].

Fig. 3b shows an overall view of the corrosion attack of an anodised and additionally 1.5 \( \mu \)m PVD-Al\(_2\)O\(_3\) coated AZ91 sample after 120 h in the salt spray test.
The test duration was five times longer than that of CrN coated sample in Fig. 3. The examination shows a widely intact surface except for some sporadic filiform corrosion. The average depth of the corrosion attack is 20 μm with sporadic maxima up to 100 μm. There is no doubt that the corrosion behaviour of plasma anodised samples is superior to CrN ones and even superior to the polished, respectively, the as casted alloy. Furthermore, the hardness of the Al₂O₃ coating seems promising for an acceptable wear resistance (Table 3).

Besides the good corrosion properties of plasma anodised samples they also must have good wear characteristics regarding a in future use in the moved component field. The wear tests set-up and the test parameters (except for the load) were the same as described before. Fig. 4 contains the results from the wear experiments at loads of 2 and 5 N. The results of the anodised and 1.5 μm PVD Al₂O₃ coated AZ91 sample was compared with AZ91-9 μm CrN, polished AZ91 and a commercial 20 μm thick anodisation on AZ91 whose high wear resistance is promoted by the supplier. The initial surface roughness of the commercial anodisation (Rₚ: 1.58 μm; Rₛ: 10.91 μm) is more than a factor 10 higher than the surface roughness of the CrN coated AZ91 (Rₚ: 0.06 μm; Rₛ: 0.98 μm) and even a factor 5–10 higher than anodised and additionally Al₂O₃ coated AZ91 (Rₚ: 0.1 μm; Rₛ: 1.98 μm).

As can be seen from Fig. 4, the CrN coated and the anodised, and Al₂O₃ coated specimens show good wear properties at a load of 2 N. Increasing the load to 5 N

Table 3
Surface hardness of different AZ91 based systems

<table>
<thead>
<tr>
<th>Coating system/surface</th>
<th>CrN</th>
<th>Plasma anodised</th>
<th>Plasma anodised + 1.5 μm Al₂O₃</th>
<th>Polished AZ91</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness HMₘₖₖₖ in GPa</td>
<td>31264</td>
<td>16691</td>
<td>2104</td>
<td>1040</td>
</tr>
</tbody>
</table>
leads to compound damage at the anodised and Al$_2$O$_3$ coated specimen. After a testing time of approximately 10 min the coating failed. It is thought, that a thicker Al$_2$O$_3$ coating is able to protect the substrate material even at higher loads on condition not to exceed the load carrying capacity of the AZ91. The wear test onto the commercial anodisations had to be aborted ahead of schedule due to crucial fretting fatigue. The wear is even higher than at polished AZ91, which completed the test run. The bad wear behaviour of the commercial anodisation can be related to its high surface roughness. Protruding edges are levelled and act highly abrasive in the contact zone. As a result of this there is no doubt that anodised and Al$_2$O$_3$ coated magnesium surfaces are superior concerning corrosion and wear behaviour in comparison with other surface treatments.

3. Summary of the results

– The parameters to produce reliable PVD hard coatings on magnesium alloys cannot be taken over from the deposition on other alloys due to the fragile and unstable thermal oxide film on magnesium, which reduces the adhesion and does not allow the formation of compressive coating stresses.

– Wear test of CrN coated AZ91 show comparable properties with other CrN coated materials. Because of its unsatisfying load carrying capability the applied area pressure for magnesium alloys is limited. Otherwise compound deformation, coating cracking and coating detachment can occur.

– In the salt spray test CrN coated AZ91 shows crucial contact corrosion caused by process related pinholes, even after 24 h testing time.

– As a suitable surface pre-treatment before the PVD deposition the plasma anodisation was developed and tested. It fulfils requirements concerning environmental, economic and technical aspects.

– Anodised and anodised plus PVD-Al$_2$O$_3$ coated specimens showed a superior corrosion behaviour in the salt spray test in comparison with PVD-CrN coated AZ91.

– After 120 h salt spray test anodised and anodised plus PVD-Al$_2$O$_3$ coated specimens showed only slight surface damage with sporadic filiform corrosion while the only CrN anodised specimen had to be removed from the test chamber ahead of schedule already after 24 h.

– Process related pinholes are assumed to be responsible for contact corrosion. Because of the area ratios the base material is exposed to extremely high anodic current densities resulting in crucial acceleration of the AZ91’s anodic dissolution.

– A non-conductive coating deposited subsequent to the plasma anodisation affects the corrosion properties in a positive way by anodically dissolving prior to the magnesium.

– Tribological testing shows acceptable wear behaviour of anodised and subsequently PVD coated specimens. The wear properties are even superior to commercial anodisations. The good wear characteristics are also related to the surface roughness, which is not affected by plasma anodisation but is crucially raised by the commercial anodisation.

References

