Electrophoretic Deposition of Aluminum on an Mg-Alloy

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ABSTRACT

Electrophoretic deposition of commercial, μm-sized Al powder was studied as an alternative method to produce an Al-rich surface on an MgAlZn alloy. The Al particles were deposited onto the surface of an Mg alloy, which represented the anode of a two-electrode-cell. Alkaline solutions were used in order to obtain negatively charged particles. A strong influence on powder deposition of the applied potential was observed in the range between +7V and +15V. Powder deposition was assisted by the formation of a hydroxide film between the particles. The process was also examined with respect to the influence of pH and deposition time.

Keywords: Magnesium, corrosion, electrophoretic deposition.

1 INTRODUCTION

Mg alloys are interesting materials for lightweight constructions. The density is substantially lower than that of Al alloys. Replacement of Al alloys by Mg alloys, however, is not possible in many cases, since the corrosion resistance of Mg alloys is inferior to that of Al alloys. Moreover, anodizing of Mg alloys, a frequently applied protection method, does not work as well as in the case of Al alloys. Generally, the corrosion resistance of Mg alloys rises with growing Al content.

For those reasons, creating of an Al-rich surface on Mg-alloys might be an interesting perspective. This Al-rich surface could serve as starting point for further surface treatments, such as anodizing in an appropriate bath for Al alloys. However, most methods for depositing Al-films have substantial shortcomings. Electrochemical deposition requires an aprotic environment, PVD layers are rather thin for corrosion protection, plasma spraying requires a sophisticated equipment. In the present work, the possibility of electrophoretic deposition of aluminum onto an MgAlZn alloy was tested as a first step of an alternative method of corrosion protection for Mg alloys.

Electrophoretic deposition is interesting for representing an inexpensive process that can be realized with a rather simple equipment. Therefore one makes use of this process in many different areas such as electrophoretic painting and the production of ceramic products. Complexly shaped freestanding objects as well as coatings and films can be produced. During electrophoretic deposition particles from a stable suspension are transferred to a surface by an electric field and are deposited there. While the transport is well understood, the deposition reaction itself is generally less understood. The particles in the suspension can be held separated by steric or by electrostatic stabilization. Steric stabilization in organic solvents of low dielectric constant occurs by the adsorption of a dispersant, for example polymer chains, which stabilize the pigments of paints. In the case of electrostatic stabilization an electrically charged double layer impedes that coagulation by attracting Van der Waals forces between the particles occurs. The stability of the suspension is influenced by a number of parameters such as the relative dielectric constant, the zeta-potential and the ion strength of the electrolyte. According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, above a critical concentration or ion strength, the attractive Van der Waals forces overcome the repulsive forces and coagulation commences. The critical concentration is high when the concentration of potential determining ions is far from the isoelectric point (IEP), and low, when the concentration is near the IEP.

Nonaqueous solutions are sometimes preferred, since they permit the application of higher voltages. In aqueous solutions, gas evolution due to the electrolysis of water can impair film homogeneity. Aqueous solutions, however, are always interesting as a less expensive and less polluting alternative. A lot of work about electrophoretic deposition was done with oxides, due to the application in the fabrication of ceramic materials. However, the process can be applied to a great variety of materials. Oxides, hydroxides, carbonates, nitrides, borides, clays, glass, polymers, and metals have already been used successfully.

Less information is available about electrophoretic deposition of metal powders. Mizuguchi has reported that deposition of aluminum powder is viable in a nonaqueous acetone – nitrocellulose solution.
In aqueous solutions, aluminum always forms an oxide on its surface. Thermodynamically, the hydroxide Bayerite is the more stable phase, however, hydroxylation of the oxide remains restricted to the surface, due to kinetic inhibition.\[5\]

The surface hydroxyl groups can be considered to be amphoteric, i.e. able to gain or to lose a proton:
\[\text{- Al – OH} + \text{H}^+ \rightarrow \text{-Al-OH}^+ \text{ or } \text{- Al – OH} \rightarrow \text{Al-O}^- + \text{H}^+.\]

In the present work, electrophoretic deposition of an industrial Al-powder with \(\mu\)m-sized particles was studied as a new alternative to produce an Al-rich film on an Mg-Al-Zn-alloy. Due to the above-described arguments, an electrophoretic behavior of the aluminum powder similar to that of Al\(_2\)O\(_3\) particles could be expected.

2 EXPERIMENTAL

The deposition was performed on an MgAlZn-alloy (AZ91HP) with the composition given in Table 1. The industrial Al-powder (Alcoa) had a purity of 99.7\%, and the following particle size distribution: +100\#: 0\%, +200\#: 0.1\%, +325\#: 11.5\%, -325\#: 88.4\%. The MgAlZn-alloy was the anode in a cell with a parallel Pt-counter electrode, positioned about 1 cm from the working electrode. The potential between working and counter electrode was applied using a power supply with potential and current control.

The isoelectric point of Al\(_2\)O\(_3\) is at \(\text{pH} \approx 9\). An alkaline solution (NaOH) was therefore used to produce negatively charged particles that can be deposited on the Mg-anode. The powder concentration was 1 g Al-powder in 90 mL of electrolyte in all tests. The powder was added to the electrolyte immediately before the beginning of the tests. The cell was open, i.e., the electrolyte was air-saturated. The specimens were mechanically polished with 1 \(\mu\)m diamond paste. The tests were performed at room temperature (about 22\(^\circ\)C). Electrophoretic deposition was studied as a function of deposition time, pH and applied voltage. The following ranges were examined: voltage: 5 V – 15 V, pH 11.5 – pH 13, deposition time 1 min – 10 min.

### Table 1: Composition of the alloy AZ91HP:

<table>
<thead>
<tr>
<th>Elemento</th>
<th>Al (%)</th>
<th>Zn (%)</th>
<th>Mn (%)</th>
<th>Fe (%)</th>
<th>Si (%)</th>
<th>Cu (%)</th>
<th>Be (%)</th>
<th>Ni (%)</th>
<th>Mg (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% (peso)</td>
<td>8,0-9,5</td>
<td>0,3-1,0</td>
<td>0,10-0,40</td>
<td>&lt;0,006</td>
<td>&lt;0,06</td>
<td>&lt;0,015</td>
<td>&lt;0,002</td>
<td>&lt;0,001</td>
<td>resto</td>
</tr>
</tbody>
</table>

3 RESULTS AND DISCUSSION

Electrophoretic deposition of the aluminum powder onto the MgAlZn-alloy has been examined as a function of pH, deposition time and applied voltage. Values between pH = 11.5 and pH = 13 were chosen, since the IEP of Al\(_2\)O\(_3\) is about 9. A pH sufficiently far from this point was desirable to guarantee the stability of negatively charged Al-particles that can be deposited on the anode. Very high pH stabilizes the Mg-alloy, however causes corrosion of the Al-particles. Fig.1 to Fig.3 show scanning electron microscopic studies of the deposited powder.

3.1 Influence of the pH.

At pH = 11.5 (Fig.1a), the surface of the MgAlZn alloy suffered a rather strong corrosion attack, with a thick layer of corrosion products covering the surface. The specimen shows an inhomogeneous distribution of the aluminum particles. The accumulation at some sites might be correlated to the microstructure of the alloy. At pH = 12.5 and pH = 13 (Fig.1b and 1c), a rather uniform distribution of the aluminum particles was achieved. The particles are embedded in a layer, which is obviously important for the binding of the particles on the surface (Fig.1d). An EDS-analysis between the particles revealed a high Al and O content, indicating that the layer is mostly aluminum hydroxide.
3.2 Influence of the Deposition Time

The influence of the deposition time was studied at 10 V and pH = 12.5. After 2 min, only a few great particles are found on the surface (Fig. 2a). The coverage of the surface rises strongly between 2 and 5 min (Fig. 2a and 2b). Between 5 and 10 min (Fig. 2b and 1b) no substantial differences are observed. The current density transients during the tests showed usually a maximum after about 1 min. The maximum value varied around 5 to 10 mA/cm². The current density diminished towards the end of the tests.

Figure 2: Al-powder, deposited with a voltage of 10 V on the alloy AZ91HP in NaOH of pH = 12.5. Deposition time: a) 2 min; b) 5 min.
3.3 Influence of the Applied Potential

The highest density of Al-particles was obtained at 10 V (Fig.1b, 1c). Higher as well as lower applied voltages showed worse results. At 5 V (Fig.3a), only localized deposition was observed. Some deposition obviously occurred along scratches while other sites might be correlated with the microstructure of the alloy. At 7 V (Fig.3b), an oxide or hydroxide film has formed on one part of the specimen, probably on the eutectic or the β-phase of the alloy. Bigger aluminum particles are imbedded in this film, while much less particles have been deposited on the rest of the specimen. The results at 15 V (Fig.3c) is similar to those at 7 V, however, the aluminum particles are imbedded in a much thicker hydroxide film.

![Figure 3: Al-powder, deposited on the alloy AZ91HP in NaOH of pH = 12.5, deposition time: 10 min. Applied voltage: a) 5 V; b) 7 V; c) 15 V.](image)

All tests were accompanied by heavy hydrogen evolution at the aluminum particles. The vehemence of the reaction increased with the increasing pH. At pH = 13, the surface of the deposited aluminum particles appears rough as a sign of the increasing corrosion attack. The high ion concentration is not favorable for the stability of the suspension. Sedimentation can be observed after longer times. However, during the rather short deposition tests this seems to be less significant. Moreover, the convection caused by hydrogen bubbling retards the sedimentation process.

The tests were usually performed with the working electrode surface in the upside position. Some tests were performed with the electrode surface in the upside down position. Deposition was similar in both cases, showing that sedimentation had practically no influence during the rather short tests. However, in the upside down position, some sites on the specimens remained blank, probably due to local blockage of the surface by gas bubbles.

There seem to be two important factors, which promote the deposition of the aluminum particles: the dissolution reaction of the aluminum particles and the electrochemical reactions occurring at the surface of the Mg-alloy.

The influence of the Mg-alloy can be confirmed by carrying out the same tests with a stainless steel anode instead of the Mg-alloy. Only a few small aluminum particles are deposited on the steel surface. The strong influence from the applied voltage of the deposition also points to the participation of the Mg-alloy. According to Huber [6], the electrochemical behavior of magnesium in solution of NaOH depends strongly on the potential. Up to 3 V he observed the formation of a very thin, light green coating. Between 3 V and 20 V, a thicker, dark grey coating is formed. This film was identified as Mg(OH)$_2$. Simultaneous O$_2$-evolution occurs in this potential range. Above this voltage, the behaviour changes again. A smooth light grey or an invisible thin film of MgO is formed. Beside the potential, the film properties depend on various other parameters, such as alloy composition and electrolyte concentration and the way, how the potential was applied, immediately or slowly.

The role of Mg(OH)$_2$ as a binder is known from literature [7], from electrophoretic deposition in suspensions that contain MgCl$_2$ or Mg(NO$_3$)$_2$. EDS-analysis of the film between the deposited aluminum particles, however, revealed, that the binder contain much more aluminum than magnesium. Probably the lowering of the pH near the surface, is the more important factor. The pH can be lowered by oxygen evolution: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{H}^+ + 2e^-$, or due to the formation of the MgO or Mg(OH)$_2$-film itself: $\text{Mg} + \text{H}_2\text{O} \rightarrow \text{MgO} + 2\text{H}^+ + 2e^-$. The lowering of the surface-pH explains the formation of Al(OH)$_3$ as binder. The lower surface-pH can also be important for the discharge of the aluminum particles. The pH at the surface probably drops to a value near the IEP of the particles and facilitates deposition. The latter effect is also used for coagulation casting, a more recent process for the production of ceramic materials.
4 CONCLUSIONS

The work has shown the possibility of creating an Al-rich surface on an MgAlZn-alloy. The density of the particles is probably high enough to fill the space between the particles by a following anodic oxidation step, adequate for aluminum alloys. The conditions for deposition suggest, that electrochemical reactions of the Mg-substrate as well as the corrosion of the aluminum particle in the alkaline solution play an important role in the deposition process.

5 REFERENCES


