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Correlation between Texture and Corrosion Properties of Magnesium Coatings Produced by PVD

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Abstract

Physical vapour deposition with energetic ions is an established technology for creating functional surfaces where changing morphologies are observed with increasing energy deposition. In this presentation, magnetron sputtering (MS) is compared with ion beam sputtering (IBS) and vacuum arc deposition (VAD) for corrosion resistant Mg coatings. With increasing average energy flux along the three methods, a transition from a columnar growth regime towards a layer-by-layer growth at increased energies was observed, while a basal texture with the c-axis normal to the surface was found in all cases. However, the full width at half maximum (FWHM) of the corresponding Mg(002) rocking curves showed a pronounced minimum of 3° for IBS deposited films, apparently caused by the reflected high energy primary Ar⁺ ions. For pure Mg films, no larger differences in the corrosion potential and the corrosion rates were measured.

1. Introduction

Magnesium is a very attractive construction material in transport industries as automotive and aerospace [1,2], due to its light weight and the highest strength-to-weight-ratio of all structural metals [3,4]. However, excessively large corrosion rates of 0.5 – 50 mm/year are presently restricting the use of unprotected magnesium alloys [5,6]. Consequently, corrosion protection is of great importance.

One approach to overcome this major problem is the design of new alloys or protective coating systems. Promising pathways towards such corrosion resistant magnesium based alloys include alloying, micro-alloying and the production of supersaturated single-phase compounds or amorphous alloys. The latter two are the most promising approaches, albeit new and innovative technologies outside the conventional casting technology are necessary to obtain phases far outside the thermodynamic equilibrium. Physical vapour deposition (PVD) processes allowing very high cooling rates (at and beyond 10^6 K/s) from the gas phase to the solid are one possibility to produce new alloys or coatings [7,8]. The advantage of the high cooling rate is the formation of homogeneous solid solution systems without precipitates as the mobility of the atoms and the allowed time for forming precipitates is strongly reduced. Furthermore, solubility limits known from conventional casting are no longer valid.

In previous works, it was shown that micro- or nano-crystalline film morphologies encompassing new alloy systems compared to conventional casting techniques can be produced [9,10]. Additionally, even components with a markedly differing melting point, such as Mg and Ti, can be congruently transferred into the vapour phase and subsequently deposited together [11]. A major factor determining the corrosion resistance of such coatings is the alloying composition [12], thus by judiciously choosing the components, a markedly reduced corrosion rate can be obtained.

Beside a minor influence of the composition on the microstructure of the coating, other process parameters - pressure, deposition angle, deposition rate, average energy per particle,

substrate – are the dominating factors. An enhanced surface mobility, e.g. by higher particle energies, can result in a transition from columnar to layer-by-layer growth [13], thus resulting in coatings with fewer defects such as pinholes. However, different amounts of internal stress may be incorporated as a secondary effect while changing the energy balance [14]. At the same time, a varying texture can be obtained. In this presentation, the influence of this film texture, obtained by using different PVD methods, on the corrosion properties of commercially pure Mg (cp-Mg) is investigated.

2. Experiment

As PVD methods, DC magnetron sputtering (MS), ion beam sputtering (IBS) and vacuum arc deposition (VAD) were employed. No additional heating was employed, thus the temperature during deposition was between room temperature and 50 °C. Cp-Mg (Mg 99.93 wt.-%, impurities: Ni, Cu, Fe, Be and Si in the ppm range) was used as a target, respective cathode in these experiments. For MS, a source power of 160 W and a target voltage of 270 V at an argon gas (purity 7.0) pressure of 0.2 Pa was used [15], while the base pressure of the ultra-high vacuum chamber was below 10^{-5} Pa. The substrates, Si and Mg, were coated under an angle of about 22.5° to the substrate normal. The target-to-source distance was about 15 cm, resulting in a deposition rate of approximately 3 – 4 $\mu\text{m/h}$ at average particle energies of 5 – 10 eV.

The ion beam sputtering experiments were performed in an UHV chamber using argon ions with an energy of 1000 eV at a working pressure of less than 0.01 Pa [16]. The angle between the ion source and the substrate normal was 45° with the target normal dividing this angle into two equal parts. The respective distances were 15 cm. Beside sputtered atoms with a kinetic energy between 1 and 5 eV, high energy backscattered Ar^+ ions were impinging on the substrate during the film deposition, yielding an average ion energy of 8 – 15 eV per deposited particle.

VAD was used as the third PVD process. At a total current of 100 A, an ion current of about 10 A could be extracted from the cathode. Using appropriate filtering techniques, macroparticles emitted from the cathode were suppressed at the expense of a reduced ion current. Average energies of 15 – 45 eV were typical for VAD. The growth rate was around 3 $\mu\text{m/h}$ for all samples.

Scanning electron microscopy (SEM) was performed to analyse the morphology while X-ray diffraction (XRD) measurements were used to identify the phase components and film texture. Information about the general corrosion properties of the coating systems and the as-cast alloys was gathered with potentiodynamic polarization measurements. The specimens were tested in 0.5 % NaCl solution at a pH of 11 using an exposed surface area of around 0.5 cm^2 . A 330 ml cell with three electrode arrangement (working, Ag/AgCl reference and Pt counter electrode) was used. The test was terminated when a corrosion current of 0.1 mA was exceeded. From the cathodic branch of the polarization curve the corrosion rate was determined using the Tafel slope.

3. Results & Discussion

Except for a thin surface layer of less than 5 nm, which is enriched with oxygen, homogeneous films were obtained, as confirmed with ion beam analysis in all cases [17]. Bulk contaminations with C, H and O are below 0.5 at.%, comparable to the purity of the sputter targets. Any influences of concentration gradients or contaminations on the microstructure and the corrosion can be excluded in the present experiments. Contamination with Ar was found for MS and IBS films at a level of 1 – 5 at.%, depending on the deposition conditions.

The microstructure of representative cp-Mg films from all three methods is shown in Fig. 1. For the first two processes – MS and IBS – the hexagonal structure is still visible, while smoother surfaces with fewer visible topological structures are formed for IBS. The total layer thickness for all these samples was about 3 μm to eliminate influences of the layer

thickness on the morphology. With increasing average ion energy from MS via IBS to VAD, a transition from columnar growth to layer-by-layer growth is observed, which is in agreement with theoretical considerations originally propagated by Thornton [8]. With increasing the deposited energy per particle, a higher (transient) mobility of the atoms impinging on the surface is obtained, thus increasing the apparent surface temperature. At the same deposition rate, the higher mobility will lead to a larger diffusivity, thus allowing a transport from the original arrival site.

The degree of preferential orientation, improving with increasing energy which could be inferred from the SEM viewgraphs was investigated with XRD in detail. For the cp-Mg films, only the hexagonal Mg phase was found with no traces of secondary phases in the scans in Bragg-Brentano geometry (see Fig. 2). At the same time, a strong preferential orientation was found with the c-plane tending to align parallel to the surface, as only reflections identified with the (002) and (004) planes were visible, beside traces of the Si(004) peak from the (100) oriented substrates. No qualitative differences have been observed for the three methods, MS, IBS and VAD:

Corresponding rocking curves centred on the Mg(002) reflection are shown in Fig. 3. In contrast, a very strong dependency on the deposition method can be inferred here. For IBS, the smallest FWHM of 3° was observed, followed by the VAD sample with 5° , whereas MS produced films with a broad, nearly bimodal distribution with a FWHM of more than 15° for the full peak. Assuming that two different components are present, slightly reduced values of $6 - 8^\circ$ are obtained.

Comparing the film morphologies presented in Fig. 1, together with the average energy per deposited particle increasing from $5 - 10$ eV for MS via $8 - 15$ eV for IBS to $15 - 45$ eV for VAD, with these rocking curves, no correlation between the morphology, resulting from the average particle energy, and the texture can be found. However, it has to be kept in mind that

the average particle energies are not representative of the whole energy distribution encountered during the deposition processes.

For VAD, no high energy particles are involved, while in MS at the present conditions, collisions will reduce the flux and the maximum energy of Ar^+ ions reflected from the cathode [18]. However, in IBS at considerably lower pressures, necessary to transport the ion beam from the source to the sputter target, the reflected primary ions will reach the substrate without further reductions in energy. As a consequence, these ions can penetrate the growing film beyond the first few monolayers. Independent of the detailed model explaining the preferential growth with either the channelling direction [19], preferential sputtering [20] or deformation energy minimization [21] determining the final texture, these energetic ions are a necessary condition for highly textured film growth.

However, a certain influence of the surface free energy of the growing Mg must be additionally present as a preferred growth of the basal planes parallel to the surface is even present at very low energy deposition. In addition, an influence of the alloying composition is also present, with Mg-Al-Zr film deposited by IBS showing a FWHM in the Mg(002) rocking curve of less than 1° [22], compared to 3° for cp-Mg in the present case. A third component determining the texture, beside the high energy particle flux and the surface energy as a function of orientation, is the structure of the substrate. For deposition on Si, covered with a native amorphous oxide layer of a few nanometer thickness, a fibre texture was found, as indicated by the (101) pole figure for cp-Mg deposited on Si by IBS in Fig. 4a. The same pole figure for a film deposited by VAD onto c-plane sapphire substrates – depicted in Fig. 4b – with a lattice mismatch of 10 – 15%, in contrast, shows a high-quality epitaxial growth.

Surprisingly, the corrosion properties show no significant influence of the process or ion energy thus of the observed texture changes. Although the corrosion rate for cp-Mg films varies between 144 and 293 $\mu\text{m}/\text{year}$ for VAD and IBS films, the potential (indicating the driving force for dissolution) is only changing from -1712 to -1739 mV being within the

typical error of ± 20 mV between different measurements on the same type of coating (see Fig. 5). However compared to as-cast Mg the corrosion potential itself is shifted by about 200 mV towards more negative values. It can be speculated whether this shift in the corrosion potential is caused by the preferred orientation of the films with the c-axis nearly normal to the surface or the increasing amount of grain boundaries. Nevertheless the variations in orientation distribution function encountered for the three methods, as presented above, do not constitute a large influence on the free corrosion potential. The effect on the corrosion rate is visible, but the calculation of the corrosion rates assume a perfect surface and the same surface area for the three processes, not accounting for the changing surface roughness as visible in Fig. 1. MS and IBS with similar surface roughness have similar corrosion rate of 260 and 293 $\mu\text{m}/\text{year}$ while the smoother VAD specimen has only 144 $\mu\text{m}/\text{year}$, suggesting that this is most likely a roughness and no texture effect.

4. Summary & Conclusions

Commercially pure Mg coatings can be deposited using different PVD techniques with the corresponding morphology closely related with the average energy per deposited particle according to the standard models for energetic film deposition. However, the texture evolution, especially the pronounced c-axis texture as measured by the FWHM of the Mg(002) reflection is highly susceptible to the high energy component delivered by reflected Ar^+ ions in ion beam sputtering. Additional influences of the substrate material and the alloying system are present.

No larger differences in the corrosion properties of the deposited films as a function of the preparation method were found, when the roughness effect on the corrosion rate is considered. Nevertheless, the significant shift of the corrosion potential of pure Mg by 200 mV towards more negative values, which allows the possibility of cathodic protection layers, has still to be accounted for. The texture change between the three deposition processes is too small to be visible in the corrosion behaviour.

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Figure Captions

Fig. 1: Surface morphology of cp-Mg films deposited by (a) MS, (b) IBS, and (c) VAD.

Fig. 2: XRD spectra measured in Bragg-Brentano geometry of cp-Mg films produced by IBS and vacuum arc deposition. The diamond symbols indicate the expected positions for Mg (PDF 35-0821).

Fig. 3: Corresponding Mg(002) rocking curves.

Fig. 4: Mg(101) pole figures for cpIBS-Mg films deposited (a) by IBS onto Si and (b) VAD onto c-axis oriented sapphire.

Fig. 5: Polarization curves for cp-Mg produced by IBS, MS and VAD (0.5% NaCl, pH11).

Fig. 1

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Fig. 2

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Fig. 3

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