Investigation of HVOF spraying on magnesium alloys

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Abstract

Magnesium alloys are promising alternatives to other lightweight alloys such as aluminum alloys due to their high specific strength and stiffness. However, the use of magnesium alloys is limited by their poor wear behaviour and corrosion performance. Recent studies have shown an enormous potential of thermal spray techniques for the surface modification of Mg alloys. The high particle velocities and moderate temperatures achieved by the High Velocity Oxy-Fuel (HVOF) flame spray process lead to very dense coatings with outstanding wear behaviour and superior bond strengths in comparison to other thermal spray processes. In this study, two Mg alloys AZ91 and AE42 were coated using the HVOF spray process. The substrates were compared in terms of the measured bond strength and the observed adhesion mechanisms of the coating. Furthermore, the coatings were characterized concerning their corrosion performance on AZ91 substrates. It was found that dense WC–Co coatings could be applied on Mg alloy substrates using the HVOF spray process. The high kinetic energy of the WC–Co particles led to a "self roughening" effect on the substrate, enabling the deposition on polished Mg alloy substrates. The coatings showed a very good adhesion to the substrates. The corrosion tests showed that the unsealed WC–Co coatings could not improve the corrosion performance of Mg alloys. In contrast, the duplex coating system with an Al bond coat improved significantly the corrosion resistance of Mg alloys. The sealed coatings showed a very good corrosion behaviour.

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1. Introduction

Magnesium alloys are promising materials for lightweight constructions such as in aircraft industry and in automobile industry due to their high specific strength and stiffness [1]. However, the use of Mg alloys is limited by their low corrosion and wear resistance. Surface treatments like anodising, painting, electroplating and conversion coatings have been conventionally used until now to improve their surface properties [2]. Among others, the high oxidising nature of Mg alloys usually demands a complex and often expensive process chain to ensure a good coating adhesion in the above mentioned processes. In addition to those conventional methods, recent studies have shown that the thermal spray technology has an enormous potential for the surface modification of Mg alloys [3–5].

The thermal spray technology offers a variety of techniques, which allow the deposition of a wide range of functional coatings designed for specific environments. Among these techniques, the High Velocity Oxy-Fuel (HVOF) flame spray process is of large significance. Today’s HVOF spray systems provide gas velocities up to 2000 m/s. The high velocities and moderate temperatures of the particles make it possible to produce very dense coatings with outstanding wear and corrosion behaviour and high bond strengths [6,7].

In this study, the application of wear protective coatings on Mg alloys using the HVOF spray process was investigated. For a better understanding of the coating bond mechanisms on Mg alloy substrates, the flattening behaviour of the splats was investigated. Additionally, the corrosion behaviour of the coated samples was investigated.
2. Experimental procedure

In this study, the most commonly used Mg alloy AZ91 and the Mg alloy AE42 with an improved creep behaviour were used as the substrate materials. As coating material, the spray powder WC–12Co −45 ± 20 μm was applied. A commercially available HVOF system DJ 2600 by Sulzer Metco was employed for deposition of the coatings. The investigated spray parameters are summarised in Table 1.

The coatings were sprayed onto flat AZ91 samples with 5 mm thickness for metallographic examination, corrosion testing and collection of single splats. Additionally, 40 mm diameter discs of AZ91 and AE42 were coated to determine the tensile bond strength of the coatings. To improve the corrosion behaviour, two approaches were tested in this study. The first one was the application of a 150 μm thick Al bond coat using an atmospheric plasma spray equipment from Sulzer Metco, the F4 gun, followed by a 200 μm thick WC–Co top layer. The second one was to apply the WC–12Co top layer directly on the substrate and close the open porosity with epoxy. To ensure an effective penetration of the sealant in the upper layers of the coating, the coating porosity was increased using a longer spray distance (40 mm more). Prior to the application of the sealant on the coating surface, the samples were cleaned with ethanol in an ultrasonic bath for 5 min and dried at 45 °C for 24 h. The sealed surface was then grinded in order to expose the coating material.

For collection of single splats, the HVOF spray gun was run quickly over the substrates. Prior to the splat tests, the surface of the AZ91 substrates was grinded and mirror-polished. The morphology of the splats was characterized by scanning electron microscopy (SEM-EDS). The microstructure of the coatings was evaluated by means of optical microscopy and the porosity was measured by image analysis using a magnification of 200×. The reported porosity values are an average of ten measurements. The bond strengths of the coatings were determined according to the European standard EN 582.

The corrosion performance of the coated AZ91 substrates was evaluated using a modified immersion test [8]. The samples were immersed in a 5% NaCl solution with a constant pH-value of 6. The increase in pH-value, resulting from the corrosion of the samples, was continuously neutralized through the addition of a 0.01 mol HCl solution. The added amount of HCl solution was recorded during the whole test for determination of the corrosion rate. The recorded curve was then fitted and the corrosion rate calculated from the deflection of the curve. In this work, the recorded curves were fitted with polynomial functions. Additionally, the samples were also evaluated using the Salt Spray Test following the norm DIN 50021 SS. All samples were tested up to failure of the coating system. Every 24 h the samples were removed from the test chamber and optically examined. The test was performed up to 14 cycles.

3. Results and discussion

3.1. Particle flattening behaviour and bond strengths of coatings

As seen in Fig. 1, the AZ91 substrate was significantly deformed by the impacting particles due to their high kinetic energy. The large deformation of the Mg substrate absorbed so much energy of the particles so that the spray particles themselves deformed less than in case of spraying them on the steel substrate. As seen in Fig. 2 (under the same spray conditions as for the Mg alloy), the steel substrate almost did not change, while
the WC–12Co particles underwent a significant flattening. In contrast, the AZ91 substrate surface was clearly blasted and only small fractions of the first spray particles adhered onto the substrate. In addition to roughening the surface, the impacting WC–12Co particles hardened the surface zone. To quantify this effect the micro-hardness of the substrate was measured along the polished cross section of the coated sample. The measurements showed that the micro hardness of AZ91 substrate decreased from $88 \pm 2$ HV$_{0.3}$ at 240 $\mu$m below the interface to the coating to a mean value of $71 \pm 4$ HV$_{0.3}$ at a depth of 740 $\mu$m (the reported values are an average of five measurements).

Fig. 3 shows the cross section of two WC–12Co coatings sprayed on AZ91 substrates with a polished surface and with a sand blasted surface, respectively. It can be seen that the WC–12Co particles cotter very well the substrate surface in both cases, thus leading to a good mechanical anchoring between the coating and the substrate. It can also be observed that the waviness at the interface of the sand blasted sample is bigger due to the greater scale roughness resulting from the sand blasting process. Similar results were observed on AE42 substrates.

In order to investigate the influence of the surface pre-treatment, both sand blasted and polished AZ 91 and AE 42 samples were coated. In all cases, the tensile adhesion of the coatings exceeded the maximal adhesion strength of the glue with a value of 40 MPa. As described in a previous work [4], the adhesion of conventionally used epoxy glues on Mg base substrates is limited to less than 50% of the adhesion strength achieved on steel substrates, thus limiting the characterisation of HVOF sprayed coatings on Mg substrates. Although the real bond strengths could not be determined, it can be seen that all the HVOF-coatings showed very good adhesion on both Mg alloys used.

Fig. 3. Cross section of a HVOF sprayed WC–Co coating on AZ91: A) polished substrate, B) sandblasted substrate.

Fig. 4. Microstructure of a HVOF sprayed WC–Co top layer, with optimized metallographic preparation to develop the coating microstructure.

Fig. 5. Cross section of an APS sprayed Al bond coat after deposition of a WC–Co top layer by HVOF.

Fig. 6. Corrosion rate in a 5% NaCl solution with constant pH.
3.2. Coating microstructure

A representative cross section of the produced WC–12Co coatings is shown in Fig. 4. A very dense coating can be seen. As reported in a previous work [9], the metallographic preparation of thermally sprayed Mg base substrates is complicated. In general it can be stated, that due to the high chemical affinity of Mg alloys, special lubricants instead of water have to be employed during the last grinding steps to avoid an extensive wear of the substrate at the interface zone. Moreover, the grinding/polishing media have to be carefully selected depending on the coating material, being diamond grinding wheels and hard silk cloths the best combination for hard coating materials. However, in spite of these preventive measures, the very different properties of the coating and the substrate materials hinder an optimal finishing of the coating by keeping a well defined interface. A compromise must be found depending on the preparation purpose. For example, the interface between the WC–Co coating and the substrate was of high priority for the samples in Fig. 3 and the Al bond coat for the sample in Fig. 5, while the microstructure of the WC–Co top layer itself was more important for the sample in Fig. 4. Therefore, Fig. 4 reveals the real microstructure of the WC–Co coating. Fig. 5 shows a cross section of a duplex coating system of an Al bond coat and a WC–12Co top layer. It is evident that the Al base layer was densified to a large extent by the impacting WC–12Co particles.

In order to increase this densification effect, the Al bond coats were pre-heated up to 160 °C with the HVOF gun, but no significant improvement of the densification was achieved. In contrast, a negative effect of the pre-heating on the adhesion of the duplex coating was observed. This was due to the high residual stresses in the coating which was increased by pre-heating the substrate. The porosity of HVOF sprayed coatings lay under 1%.

Fig. 7. Overview of samples after salt spray test: A) 200 μm thick WC–Co coating after 7 h, B) 200 μm thick WC–Co coating after 1 cycle of 24 h, C) duplex coating after 6 cycles and D) sealed WC–Co coating after 14 cycles.

Fig. 8. Cross section of the sample coated with the duplex layer (Fig. 7C) after 6 cycles in salt spray test.
3.3. Corrosion behaviour

By means of the modified immersion test with a constant pH-value, it is possible to compare qualitatively the corrosion behaviour of the coated AZ91 substrates. Fig. 6 shows the corrosion rate over the test duration for samples coated with either a single 200 μm thick WC–12Co top layer or a duplex coating system consisting of a 150 μm thick Al bond coat and a 200 μm thick WC–Co top layer. As it can be seen, the deposition of a single WC–12Co top layer actually affects negatively the corrosion behaviour of the AZ91 substrate, leading to higher corrosion rates in comparison to the uncoated substrate. After approximately 3 h test, the measured corrosion rate increased abruptly, indicating the failure of the coating. From this time point, the substrate got in direct contact with the electrolyte. It must be pointed out, that the corrosion rate measured from this moment did not correspond to the real corrosion behaviour of the sample, because the maximal feeding capacity of the HCl was already exceeded, not allowing to keep the pH constant. The WC–12Co top layers as a whole were very dense, but may present some local defects, which impede an effective isolation of the substrate. At such locations, galvanic cells can be formed between the substrate and the coating, thus leading to the detrimental effect on the corrosion behaviour observed on coated samples in comparison to the uncoated substrate. In contrast, it can be seen that the duplex coating system improved significantly the corrosion performance. The densified Al bond coat offered a good isolation function.

By the salt spray test, the samples were tested until failure of the coating in the form of localised corrosion attack or coating delamination. Fig. 7 shows an overview of the coated samples after the test. In accordance with the previous results, the samples coated with single WC–12Co layers showed also a very poor corrosion performance. They were already damaged after a few hours test, showing isolated corrosion damages as seen in Fig. 7A. It supports the hypothesis that local coating defects may allow the formation of isolated galvanic cells.

The duplex coating system showed again a much better performance. The samples showed the first corrosion damages after 6 test cycles. After a detailed characterisation of the cross section of the sample, it is evident that the duplex coating remained almost intact after the test and mainly the substrate is being corroded (see Fig. 8).

The sealed coatings showed the best performance, overcoming the 14 test cycles. The investigation of the cross section of the samples showed that the sealant could effectively close the open porosity of the upper layer of the WC–Co coating and the interface showed no evidence of corrosion (see Fig. 9).

4. Conclusions

The results in this study show that wear resistant WC–12Co coatings with high bond strengths could be applied on Mg alloy substrates by the HVOF spray process. The high kinetic energy of the WC–12Co particles led to a “self roughening” effect on the substrate, enabling the deposition of WC–12Co coatings on polished Mg alloy substrates with high bond strengths. The real bond strengths could however not be determined because of the failure of the epoxy glue. The corrosion tests showed that unsealed WC–Co coatings led in fact to a detrimental effect on the corrosion performance of Mg alloys. The corrosion performance of the system can be significantly improved employing an Al bond coat. Furthermore, the application of an organic sealant like epoxy can be an effective method to prevent the corrosion of Mg substrates coated with WC–Co in Cl−-containing environments.

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