Investigation of particle flattening behaviour and bonding mechanisms of APS sprayed coatings on magnesium alloys

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Abstract

Magnesium alloys are promising alternatives to other lightweight materials due to their high specific strength and stiffness. However, the use of magnesium alloys is limited by their poor wear behaviour and low corrosion resistance for many industrial applications. The thermal spray technology offers a wide range of possibilities to improve the surface properties of Mg-based components. In this study, three different coating materials, namely Al, NiAl5 and Al2O3, were applied on AZ91 and AE42 substrates using the atmospheric plasma spray technology. The investigation was focused on the bonding strength of the coatings and the related bonding mechanisms. For a better understanding of the bonding mechanisms, the flattening behaviour of the spray particles was investigated in correlation with the substrate pre-heating temperature. It was found that NiAl5-particles could well melt the substrate at the surface and deformed it locally; Al-particles did the same but to a lower extent. The dominating bonding mechanism for NiAl5-coatings could be attributed to a metallurgical bonding. For Al-coatings, this mechanism played a more important role once the substrate pre-heating temperature was increased. Al2O3 particles in contrast, were less able to deform the substrate in spite of their higher thermal load and the mechanical anchoring remained the main bonding mechanism. The thermo physical properties of the Mg substrate showed also to have an influence on the adhesion of the coatings.

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Keywords: Magnesium alloys; APS spraying; Flattening behaviour; Adhesion

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 currently limited by their low corrosion and wear resistance. Surface treatments like anodising, painting, electroplating and conversion coatings have been conventionally used to improve their surface properties [2]. However, the high oxidising nature of Mg alloys usually demands a complex substrate pre-treatment to ensure a good coating adhesion and the solutions offered by these processes are often limited. Furthermore, in spite of the successful embrace of environmentally conscious manufacturing principles over several years, the release of hazardous chemical wastes, e.g. by electroplating, is still one of the major concerns.

Thermal spray technology offers a variety of techniques, which allow the deposition of a wide range of functional coatings designed for specific environments. Recent studies have shown the enormous potential of thermal spray techniques for the surface modification of Mg alloys [3–7]. Although some attempts have been done to characterize the adhesion of coatings sprayed by atmospheric plasma spraying (APS) [6,7], the dominating adhesion mechanisms have not been well understood until now.

This study was carried out to determine the bond strengths of different APS sprayed metal and ceramic coatings on Mg alloy substrates and to characterize the dominating bonding mechanisms by studying the flattening behaviour of the particles in correlation with the substrate pre-heating temperature. To cover a wide rage of relevant industrial applications, the deposition of two metal powders with significantly
different melt temperatures and one ceramic powder was investigated.

2. Experimental procedure

In this study, the most commonly used Mg alloy, AZ91, and an alloy with improved creep properties, AE42, were used as substrate materials (see the composition of the substrates in Table 1). As coating materials three different spray powders were used: NiAl5 –90+45 μm, Al (99%) –90+45 μm and Al2O3 –45 μm+5.5 μm. A commercial APS system with the plasma gun F4 produced by Sulzer Metco was used for the deposition of the coatings. The parameters used are listed in Table 2.

The coatings were deposited onto 5 mm thick flat specimens for metallographic examination and collection of single spray splats. Additionally, 40 mm diameter discs were coated to determine the tensile adhesion strength of the coatings according to the European standard EN 582. To avoid the influence of the substrate temperature on the flattening behaviour of the splats, some measurements on pre-heated substrates were carried out. For this purpose, the substrates were heated-up from the rear side using a hot stream of air. The substrate temperature was measured using a thermocouple type k fixed in a bore at the side of the sample.

3. Results and discussion

3.1. Flattening behaviour of the spray particles

Fig. 1 shows the collected NiAl5 splats. It can be seen in Fig. 1(a) and (b) that the surface of the AZ91 substrate was melted due to the heat transferred from the impacting NiAl5 particle, leading to the formation of the so called “flower type” splat morphology [8]. The contours of neighboring “petals” matched almost perfectly with each other. Therefore, it can be supposed that those petals came from the same solidified splat, which broke up during cooling. The already solidified fractions swam over the molten substrate surface and were separated by the moving melt. In contrast to the report in [8], the splat in Fig. 1(a) solidified in form of a ring instead of a cake, so that the center part of the resulting flower type splat showed no powder material. The formation of similar ring type splats without substrate melting is associated to the high kinetic energy of the particles, which leads to a sort of recoil of the melt [9]. In contrast, smaller particles with lower kinetic energies used to break up during cooling. The already solidified fractions swam over the molten substrate surface and were separated by the moving melt. In contrast to the report in [8], the splat in Fig. 1(a) solidified in form of a ring instead of a cake, so that the center part of the resulting flower type splat showed no powder material. The formation of similar ring type splats without substrate melting is associated to the high kinetic energy of the particles, which leads to a sort of recoil of the melt [9].

To investigate the influence of the substrate temperature on the flattening behaviour of the splats, some measurements on pre-heated substrates were carried out. For this purpose, the substrates were heated-up from the rear side using a hot stream of air. The substrate temperature was measured using a thermocouple type k fixed in a bore at the side of the sample.

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Other than the NiAl5 particles, the flattening behaviour of Al particles was substantially influenced by the substrate temperature (Fig. 3). Without pre-heating, only very few particles adhered to the substrate surface, while pre-heating the sample already at a temperature of 160 °C many splats can be observed. A similar dependence on the substrate temperature can be observed for Al2O3 splats. Without pre-heating almost no particles adhered to the substrate, while with a pre-heating to 160 °C, clearly more splats were collected. However, in this

Table 1
Composition of the substrates

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Al</th>
<th>Zn</th>
<th>Mn</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Ni</th>
<th>Others</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ91</td>
<td>9.14</td>
<td>0.86</td>
<td>0.31</td>
<td>0.035</td>
<td>0.001</td>
<td>0.003</td>
<td>&lt;0.001</td>
<td>&lt;0.02</td>
<td>Bal.</td>
</tr>
<tr>
<td>AE42</td>
<td>3.5–4.5</td>
<td>Max. 0.2</td>
<td>Min. 0.1</td>
<td>Max. 0.1</td>
<td>&lt;0.005</td>
<td>&lt;0.02</td>
<td>&lt;0.002</td>
<td>&lt;0.02</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Table 2
Spray parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Al 99%</th>
<th>NiAl5</th>
<th>Al2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2 [l/min]</td>
<td>4</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>Ar [l/min]</td>
<td>35</td>
<td>40</td>
<td>38</td>
</tr>
<tr>
<td>Current [A]</td>
<td>450</td>
<td>550</td>
<td>600</td>
</tr>
<tr>
<td>Stand-off distance [mm]</td>
<td>110</td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>Carrier gas N2 [l/min]</td>
<td>3.7</td>
<td>2.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Feeding rate [g/min]</td>
<td>15</td>
<td>23</td>
<td>16</td>
</tr>
<tr>
<td>Cooling-compressed air [bar]</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Relative gun velocity [mm/s]</td>
<td>500</td>
<td>500</td>
<td>600</td>
</tr>
</tbody>
</table>
case splats with an almost perfect disk shape can be observed, as shown in Fig. 4. For a detailed characterization of the splat morphology, the penetration depth of the splats was measured by laser profilometry. In addition, the cross section of the splats was metallographic prepared and measured by means of image analysis. Fig. 5 shows the typical cross section and profile of NiAl5 splats sprayed on AZ91 without substrate pre-heating. It is evident that the substrate underwent a strong deformation as result of the particle impact, leading to the formation of a crater.

Fig. 1. APS sprayed NiAl5 splat on AZ91: a) SE- and b) BSE-micrograph of flower type splat, c) BSE-micrograph of splashed splat.

Fig. 2. APS sprayed NiAl5 splats on AZ91 at different pre-heating temperatures.
The penetration depth was measured as a characteristic feature of the splats. The deepest point in the splat center was measured as representative crater depth. The measured values are showed in Fig. 6, where no values are reported for ceramic splats collected on substrates without pre-heating, since only a small fraction of the particles remained attached to the substrate, not allowing reliable measurements. It can be seen that the depth of the crater for all investigated coating materials increased with the pre-heating temperature of the substrate. The metallic particles showed larger penetration depths than the ceramic particles. Between both investigated metal powders, the deepest craters were formed by NiAl5 particles.

It is evident that the physical properties of the particles play a decisive roll determining their thermal interaction with the substrate and thus their flattening behaviour on the substrate surface (see Table 3). Ignoring the thermal load transferred from the jet flow and assuming that solidification starts after flattening, the surface temperature of the substrate reached as result of the impact of the molten particles can be estimated following the approximation of Dallaire [10], which takes into account the solidification of the spray droplet and the melting of the substrate. The substrate will theoretically melt if the resulting surface temperature reaches the melting point of the Mg substrate. Fig. 7 shows the calculated particle–substrate

Fig. 3. APS sprayed Al splats on AZ91 at different pre-heating temperatures.

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Fig. 4. Al2O3 splats on AZ91 pre-heated at 160 °C: a BSE-overview and b detail of a.
temperature profiles for Al–, NiAl5– and Al2O3 splats 2 and 10 μs after the impact on the Mg substrate. The calculations were performed using the particle temperature measured by in-flight pyrometry as reference (Al: 2400–2500 °C; NiAl5: 2300–2400 °C; Al2O3: 2700–2800 °C). Although the values measured by in-flight pyrometry correspond only to the surface temperature of the particles and especially the average temperature of the metal particles could be indeed lower, it can be stated that even the Al particles are by far able to melt the Mg substrate if there is a good physical contact between the splats and the substrate.

Since the wettability of the substrate by the molten droplets use to be significantly improved with the temperature, it can be expected that an increase in the substrate temperature would lead to a better physical contact and thus to a lower thermal resistance between the splats and the substrate [13,14]. The observed correlation between the crater depth and the substrate pre-heating temperature could thus be mainly attributed to an increase in the heat affected zone in the substrate resulting from the more efficient thermal transfer.

If a perfect contact between the flattened splat and substrate is given, the transient heat conduction into the substrate will be mainly determined by the thermal effusivity $e$ of the particle material (formally defined as $(k \rho c_p)^{1/2}$, where $k$ is the thermal conductivity, $\rho$ the density and $c_p$ the specific heat capacity) and the amount of heat stored in the particles. For the Al2O3 particles, one can additionally expect that the solidification will start earlier and may have a strong contribution to the transient heat behaviour at the interface. However, in spite of their higher latent heat and in-flight temperature, the Al2O3 particles are theoretically less able than the Ni particles to heat-up and melt.

<table>
<thead>
<tr>
<th>Property</th>
<th>Al</th>
<th>Ni</th>
<th>Al2O3</th>
<th>AZ91</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density [g/cm³]</td>
<td>2.70</td>
<td>8.91</td>
<td>3.98</td>
<td>1.81</td>
</tr>
<tr>
<td>Heat conductivity [W/m.K]</td>
<td>237</td>
<td>91</td>
<td>39</td>
<td>72</td>
</tr>
<tr>
<td>Specific heat Cp [J/Kg.K]</td>
<td>928</td>
<td>440</td>
<td>775</td>
<td>1050</td>
</tr>
<tr>
<td>Latent heat of fusion [KJ/Kg]</td>
<td>396</td>
<td>298</td>
<td>1070</td>
<td>373</td>
</tr>
<tr>
<td>Thermal expansion coeff. $\alpha$ [$10^{-6}$ K⁻¹]</td>
<td>23</td>
<td>13</td>
<td>8</td>
<td>26</td>
</tr>
<tr>
<td>Melting point [°C]</td>
<td>660</td>
<td>1455</td>
<td>2054</td>
<td>470–598*</td>
</tr>
</tbody>
</table>

* Taking the liquidus temperature as reference.
the Mg substrate, since they have a much lower thermal effusivity. In the lowest level are the Al particles, with a relatively high effusivity but a lower volumetric heat capacity than the Ni and the Al₂O₃ particles.

On the other hand, the degree of deformation induced in the substrate will also be significantly affected by the kinetic energy of the particles. In principle, the Al₂O₃ particles are closely as able as the Ni particles to heat up the substrate, however, since most of their kinetic energy may be spent in overcoming the viscous friction, the overall kinetic energy transferred to the substrate should be fairly small. Therefore, in spite of their relatively high in-flight velocities (320–340 m/s), the Al₂O₃ particles are less able to deform the Mg substrate than the NiAl₅ and Al particles with moderate velocities, 160–180 and 200–220 m/s respectively.

Concerning the different splat morphologies, the sudden improvement on the flattening behaviour of Al₂O₃ splats can be mainly attributed to their faster solidification in comparison to the investigated metallic materials. As result of the better physical contact and thus to the more efficient thermal transfer at higher substrate temperatures, the Al₂O₃ splats can solidify particularly fast, what represents a significant increase on the viscous forces and hinders the splashing of the melt [13]. According to the calculations, Al₂O₃ splats with an average thickness under 5 μm would be already solidified 2 μs after the impact on the Mg substrate. In contrast, the upper part of the metallic splats remains quite longer far over its melting point and the melt is fluid enough to flow over the solidification front. It would explain why the splashing of metallic particles can not be avoided even by increasing the substrate pre-heating temperature at those investigated spray conditions.

### 3.2. Adhesion strength

The tensile adhesion strengths of the coatings are shown in Fig. 8. The tensile strength of the NiAl₅ coatings was between 17 and 25 MPa, far over those values measured for Al (6–15 MPa) and Al₂O₃ coatings (5–7 MPa). In the case of the NiAl₅ coatings, a pre-heating of the sand blasted substrate to 160 °C led to an increase of the tensile strength by more than 40%. The same tendency can be seen but to a less extent for Al and Al₂O₃ coatings. In the case of the Al₂O₃ coatings, the higher mismatch between the thermal expansion coefficient of the coating and the substrate led apparently to very high residual stresses in the coating, limiting its adhesion strength.

In order to have a better understanding of the dominating bonding mechanisms some measurements were carried on polished substrates. In the case of NiAl₅ coatings, the adhesion achieved on polished AZ91 substrates without preheating exceeded clearly the values obtained on those blasted substrates. This indicates that the main bonding mechanism was based on metallurgical bonding due to melting of the substrate surface as shown above. The reduction of the adhesion strength by sand blasting could be attributed on the one hand to the worse flattening behaviour of the splats on the roughened substrate surface and the lower thermal transfer, thus reducing the metallurgical bonding. On the other hand, the rest of corundum particles from grit-blasting could also lead to a decrease of the contact surface between the splats and the substrate, affecting the effective bonding surface. The effect of the substrate pre-heating is also reflected on the adhesion strength on polished substrates. In contrast to the NiAl₅ coatings, the adhesion strength of Al coatings on polished substrates was lower than those of the coatings on the blasted samples, as usually could be expected. In agreement with the results presented above, at room temperature the molten Al particles are less able to wet and melt the Mg substrate and the dominating bonding mechanism could be linked to the mechanical anchoring of the splats. It is evident that the substrate preheating increased the physical contact between the Al splats and the substrate, thus leading to higher adhesion strengths by pre-heated-polished samples in comparison to blasted substrates coated at room temperature. The Al₂O₃ coatings in contrast, do not adhere to the polished surfaces and the mechanical anchoring may be thus the decisive bonding mechanism.

In addition, it can be seen that the substrate materials affected also the adhesion strength of the coatings. In general, higher adhesion strengths were obtained on the AE42 substrates in comparison to the coatings deposited on the alloy AZ91. This can be attributed to the lower thermal expansion coefficient of the AE42 alloy at temperatures over 120 °C [11] compared to AZ91, which could reduce the residual stresses in the coating.

### 4. Conclusions

In this study, the flattening behaviour of three different particles materials on AZ91 substrates at different pre-heating temperatures was investigated. The penetration depth was measured as characteristic feature of the splats. The adhesion strength of the corresponding coatings was examined. It has been shown, that the physical properties of the particles play a decisive roll determining their thermal interaction with the substrate and thus their flattening behaviour on the substrate surface. It was found that NiAl₅-particles are able to locally melt the substrate surface and deform it substantially. The metallurgical bonding may be the responsible mechanism for the good adhesion strengths observed for NiAl₅ coatings even on polished substrate surfaces. Al₂O₃ particles may be, in principle, almost as able as the NiAl₅ particles to melt the Mg
substrate; however, they do not deform it and adhere only poorly on blasted substrate surfaces. Even if having a much lower volumetric heat capacity and kinetic energy, the Al particles are by far able to melt and deform the Mg substrate if a good contact between the splats and the substrate is given.

The preheating of the substrate may significantly improve the adhesion strength of the coatings. It was observed that for all investigated coating materials the crater depth produced by the spray particles increased with the pre-heating substrate temperature. It could be mainly attributed to an increase in the heat affected zone in the substrate as result of a better physical contact between the splats and the substrate and thus of a more efficient thermal transfer. In addition, the thermo physical properties of the Mg alloy seem also to influence the adhesion strength of the coatings.

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