Plasma Sprayed Alumina-Titania Based Coatings on Magnesium Substrates

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In this study, pure alumina, titania and alumina 3% titania ceramics are deposited on magnesium substrate by plasma spray technique. The coatings were characterized by means of scanning electron microscopy (SEM), and x-ray diffraction (XRD). In the plasma spray coating, lamellar structures are formed as a result of the deformation of the melt semi-melt particles hitting the substrate and the solidification of the particles. As a result of the XRD analysis, Mg, Al₃Mg, Ti₅O₆, Ti₆O₁₁, (Mg₀.₆Ti₂.₄)O₅ and MgTi₂O₅ peaks were determined. The average hardness values of the samples coated with TiO₂, Al₂O₃, Al₂O₃+TiO₂ and TiSZ were measured as 921 HV₀.₁, 902 HV₀.₁, 914 HV₀.₁ and 1030 HV₀.₁ respectively. The hardness of the coatings is 16-18 times higher than the substrate.

Keywords: Plasma spray coating, magnesium, TiSZ, microhardness

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1. Introduction

Magnesium (Mg) and its alloys are the lightest engineering materials and this properties makes it one of the possible candidate materials in many fields. They are attracted more attention for their low density, high specific strength and good vibration and sound damping properties. However, poor corrosion and wear resistance limits its application. It is the easiest method to coat the magnesium and its alloys to increase the corrosion resistance [1]. Many different coatings are produced on magnesium based materials by different methods. Plasma spray provides high quality ceramic coating with the easy processing. Plasma spray ceramic coatings have high adhesion-cohesion strength. Furthermore, coatings do not need post-processes such as heat treatment etc.. However, due to the high plasma temperature, it may be difficult to control the phase structure and purity of the sprayed material during the coating process. In addition, materials with low vapor pressure can evaporate in the plasma plume and non-stoichiometric coatings can be formed [2,3].

Alumina ceramics are widely used in aggressive service conditions with their high temperature resistance,
fracture toughness, good abrasion resistance and good chemical stability. Alumina is one of the most industrially produced coatings with plasma spray. Therefore, plasma spray alumina coatings have been the subject of many investigations [4]. According to these studies, when alumina is sprayed with plasma spray, phase transformations occur due to high plasma enthalpy. Commercial alumina powders are produced in alpha alumina phase. However, delta and gamma alumina phases may occur due to phase transformation in coatings according to plasma spraying conditions. The general approach is that these phases do not significantly affect the coating characteristics. However, in some studies, it has been reported that these phases adversely affect the coating corrosion resistance [5].

Titania is another one of the most widely used ceramics as a coating material with its dielectric, mechanical and chemical properties. When titania is sprayed with plasma, it may be decomposed depending on process parameters and sub oxides may form. Therefore, different phases occur in the O/Ti ratio. Researchers have reported that this ratio is highly effective on the corrosion resistance of the Coating [6,7]. Titanium is added between 3 and 40% in order to improve the corrosion resistance of alumina ceramics against dilute acids. This process forms a phase in the Al2TiO5 composition in the coating structure [8]. Therefore, the coating structure also includes the Al2TiO5 phase, except the alumina and Titania phases. This complex phase composition significantly affects the coating properties and provides extra corrosion resistance [9].

The aim of this study is to produce TiO2, Al2O3 and Al2Ti3O7 coatings by plasma spraying method on the surface of Mg and to examine the effect of the coating layer on microstructure and microhardness properties. Microstructure and phase properties were determined by scanning electron microscopy (SEM), energy dispersion spectrometry (EDS) and X-ray diffractogram (XRD) analyzes. The change in microhardness was measured along a line from the coating zone to the substrate.

### 2. Experimental Studies

Magnesium was used as the substrate with the shape of 1 cm² and thickness of 2.5 mm. The EDS analysis results of taken from two different points on Mg substrate was given in Table 2.1. Prior to coating production, the substrate was grit blasted using 50-80 mesh alumina particles, to clean the sample surface and increase surface roughness. The grit-blasted substrate was then cleaned by ultrasonic cleaner to remove residual entrapped grit.

#### Table 2.1. Chemical composition of Mg substrates

<table>
<thead>
<tr>
<th>Substrates</th>
<th>C</th>
<th>O</th>
<th>Mg</th>
<th>Mn</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>14.02</td>
<td>3.42</td>
<td>81.78</td>
<td>0.78</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>14.48</td>
<td>5.40</td>
<td>79.40</td>
<td>0.72</td>
<td>100.0</td>
</tr>
</tbody>
</table>

After the pre-fabrication process, substrates were fastened in a turntable. Commercially available Metco 105NS Al2O3, Amdry 6510 TiO2, and Amdry 6200 Al2O3 3TiO2 powder was sprayed using the atmospheric plasma spray method by Metco 9MB plasma spray gun. The gun nozzle is a 730°C and powder injection angle was placed perpendicular to plasma flame. Process parameters of plasma spray are listed in Table 2.2.

#### Table 2.2. Process parameters for plasma spray

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current (A)</td>
<td>500</td>
</tr>
<tr>
<td>Primary gas flow rate, AR (scfh)</td>
<td>90</td>
</tr>
<tr>
<td>Secondary gas flow rate, H2 (scfh)</td>
<td>15</td>
</tr>
<tr>
<td>Carrier gas flow rate, Ar (scfh)</td>
<td>13.5</td>
</tr>
<tr>
<td>Spray distance (mm)</td>
<td>65</td>
</tr>
<tr>
<td>Turntable speed (Hz)</td>
<td>40</td>
</tr>
</tbody>
</table>

After plasma spray process, metallographic processes were applied to obtain images by scanning electron microscope (SEM). These applied metallographic processes were applied as sanding and polishing respectively. The surfaces of the samples taken on the surface were sanded with 200, 400, 600, 800, 1000 and 1200 mesh abrasives respectively. The surfaces of the samples were then polished with 3 and 1 diamond suspensions respectively. The scanning electron microscope (SEM) images were taken from FEI QUANTA 250 FEG u device in Kastamonu University Central Research Laboratories. XRD measurements of the produced samples were made with Bruker D8 Advance brand. Measurements were made at Kastamonu University Central Research Laboratories. The microhardness measurements was performed by using SHIMADZU brand HMV-G21 model microhardness measurement device. Under HV0.025 and HV0.1 kg load in Kastamonu University Metallurgical and Materials Engineering Laboratory. Micro hardness measurements were made by applying a load of 0.025 and 0.1 kg for 10 seconds.

### 3. Result and Discussion

#### 3.1. SEM reviews of coatings
Plasma spray spraying method was used to produce TiO$_2$, Al$_2$O$_3$ and Al$_2$O$_3$ based coatings on the surface of Mg. It is aimed to improve the surface properties after coating. It is aimed to improve the microstructure and mechanical properties of the Mg material with the coatings made on the Mg surface.

When the SEM images given in Figure 3.1 are examined, samples that have been coated by the plasma spray spray method are seen. When the given SEM images were examined, the coatings were successfully coated on the Mg base by the plasma spray spray method. It is clearly seen that the coatings produced with plasma spray coating have structures that are parallel to each other, ie lamellar structures. In the plasma spray coating, lamellar structures are formed as a result of the deformation of the melt semi-melt particles hitting the substrate and solidification of the particles there [10]. Plasma spray coatings usually contain pores, oxides, insoluble or semi-melt grains and inclusions [11]. As can be seen from the SEM microstructures, the coatings showed a lamellar solidification parallel to the substrate. This is the result of the well-known in plasma spray coatings that molten metal droplets hit the substrate, precipitate and solidify during impact [12-14]. SEM images taken from the produced coatings are given in Figure 3.1.

**Figure 3.1.** SEM images of the coatings; a) Uncoated Mg, b) TiO$_2$, c) Al$_2$O$_3$, d) Al$_2$O$_3$ + TiO$_2$

### 3.2. SEM-EDS analysis of coatings

SEM-EDS analyzes taken from Mg base material are given in Figure 3.2.

**Figure 3.2.** SEM-EDS analysis of uncoated base Mg material

SEM-EDS analyzes taken from samples coated with TiO$_2$, Al$_2$O$_3$, Al$_2$O$_3$ + TiO$_2$ and TiSZ on the surface of Mg are given in Figure 3.3. When the analysis results given in Figure 3.3 are examined, it is understood that the basing material is Mg and the coating materials are TiO$_2$, Al$_2$O$_3$, Al$_2$O$_3$ + TiO$_2$ and TiSZ.

**Figure 3.3.** SEM-EDS analysis of the coated samples; a) TiO$_2$, b) Al$_2$O$_3$, c) Al$_2$O$_3$ + TiO$_2$

When the analysis results given in Figure 3.3 are examined, the Al, Mg, Ti, Zr and O peaks that are also present in the coatings can be seen clearly.

### 3.3. XRD analysis of coatings

XRD graphics of TiO$_2$, Al$_2$O$_3$, Al$_2$O$_3$+TiO$_2$ and TiSZ based coatings produced by plasma spray spraying method are given in Figure 3.4.
When the XRD graphs given in Figure 3.4 are examined; Mg, AlMg, Ti₅O₆, Ti₆O₁₁, (Mg₀.₆Ti₂.₄)O₅ and MgTi₂O₅ peaks were detected. The contact areas between the two oxides are very large due to their grain size. Therefore, it is natural for AlMg, Ti₅O₆, Ti₆O₁₁, (Mg₀.₆Ti₂.₄)O₅ and MgTi₂O₅ to be formed during plasma spraying. Homogenized powders also allow homogeneity of the coating [15].

3.4. Microhardness analysis of coatings

The microhardness measurement tests of the coatings were carried out in the "HMV-G21" model microhardness measuring device of the "SHIMADZU" brand by applying 25 and 100 grams with a waiting time of 10 seconds. The microhardness graph of the coating samples is given in Figure 3.5.

![Figure 3.4. XRD Graphics of Coatings](image)

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![Figure 3.5. Microhardness graph of coatings](image)

Figure 3.5. Microhardness graph of coatings

Hardness measurements were taken along a line from the substrate and coating regions. The hardness of the substrate was measured at approximately 55 HV₀.₀₂₅. The hardness of the coating layer varied depending on the coating layer in the range of 902-1030 HV₀.₁. The average hardness values of the samples coated with TiO₂, Al₂O₃, Al₂O₃+TiO₂ and TiSZ were measured as 921 HV₀.₁, 902 HV₀.₁, 914 HV₀.₁ and 1030 HV₀.₁ respectively. The hardness of the coatings is 16-18 times higher than the substrate. It has been interpreted that the hardness increased due to the high proportion of non-melting grains in the coating or the grain size morphology [15].

4. Conclusion

Plasma spray spraying method has been successfully applied in the production of TiO₂, Al₂O₃ and Al₂O₃ based coatings on the surface of Mg. In the experimental studies obtained;

- It was determined that the coatings were successfully coated on the Mg substrate by the plasma spray spray method in SEM images. It has been clearly seen that the coatings produced by plasma spray coating have structures that are parallel to each other, ie lamellar structures.
- The result of XRD analysis, the Al, Mg, Ti, Zr and O peaks that are also present in the coatings can be seen clearly.
- The XRD graphs; Mg, AlMg, Ti₅O₆, Ti₆O₁₁, (Mg₀.₆Ti₂.₄)O₅ and MgTi₂O₅ peaks were detected.
- The average hardness values of the samples coated with TiO₂, Al₂O₃, Al₂O₃ + TiO₂ and TiSZ were measured as 921 HV₀.₁, 902 HV₀.₁, 914 HV₀.₁ and 1030 HV₀.₁ respectively. The hardness of the coatings is 16-18 times higher than the substrate.

References


