Mechanical Properties and Electrochemical Corrosion Behaviour of TiSZ-Reinforced Hydroxyapatite Coatings on Magnesium Substrate with Titanium Interlayer

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Abstract

In this study, pure and 10% wt. TiSZ-reinforced HA coatings were deposited on magnesium substrate using plasma spray as a single layer and double layer with a HVOF sprayed Ti bond coat. The coated specimens were characterized by X-ray diffraction (XRD) analysis, and scanning electron microscopy (SEM, EDS). Rockwell-C adhesion and scratch tests were performed. The corrosion behaviours in simulated body fluid (SBF) of coatings were investigated by an electrochemical corrosion test. The microscopic observation shows that a dense, continuous Ti buffer layer and bioceramic HA, and HA+TiSZ coatings were produced successfully. The presence of the Ti intermediate layer reduced the corrosion rate of the bioceramic coatings. The double-layer HA-Ti coating on the magnesium substrate is more resistant to corrosion than the single-layer HA coating. Rockwell-C adhesion tests show that adhesion of coatings improves with the addition of TiSZ. Reinforcing HA with TiSZ negatively affected the scratch resistance of the coatings. The effect of the Ti bond layer on adhesion and cohesion behaviour of coatings is not significant.

1. Introduction

Many metallic materials such as stainless steel, titanium and its alloys, and Co-Cr alloy have been used in the production of biomedical implants. These materials are expected to have good corrosion resistance, consistent mechanical and physical properties with bone tissue, and self-controlled degradation in the body. Good corrosion resistance ensures that these materials do not cause toxic or allergic effects since their dissolving in the body and preventing the release of harmful elements. In addition, the mechanical and physical properties of the permanent implants are lost due to the corrosive environment inside human body and implants need to be replaced through surgical operations. This operation risk patients life and bring about high cost. In addition, the density difference between the materials used in implant manufacturing and the bone tissue and young module mismatches cause by stress shielding. The implant screw is loosened and unable to function due to bone resorption [1, 2].

Due to these problems, the search for more efficient materials for implant applications continues. Mg and its alloys are used in the research of alternative implant material due to the low-density, young module that is close to the bone tissue. In addition, Mg is one of the elements that the body needs, and it is abundant in bone tissue [3-6]. Mg ion release can accelerate the formation of bone tissue. However previous studies have shown that corrosion resistance of bare Mg and its alloys is not sufficient for implant applications. As a result of the corrosion of Mg and its alloys, the evolution of hydrogen gas in aqueous solutions such as body fluid and alkalization have been reported. In addition, the excessive loss of Mg in the implant materials due to corrosion causes the implant to lose its mechanical stability early on [3, 7-10].

The corrosion resistance and biocompatibility of Mg and its alloys can be improved by depositing protective bioceramic coatings upon them.[11-13]. Hydroxyapatite (HA) coatings are widely used in
biomedical implant applications. These coatings increase the corrosion resistance of the implants as well as accelerate tissue growth due to their physical and chemical properties. Different techniques are used in the production of HA coatings. Plasma spray is one of the most well-known methods due to its unique porous coating microstructure. The porosity of the coating structure is extremely important for the adaptation of the implant to the tissue[14-16].

Plasma-sprayed HA coatings can have a porosity between 3% and 20%. The high-porosity ratio promotes biocompatibility and tissue growth but extreme weakening in mechanical properties such as stiffness and elastic modulus. With high-porosity coatings, coating integrity is easily lost due to cracking, degradation and delamination in aggressive body fluids.

Corrosion resistance of highly porous HA coating is also weak. Complete porosity control for plasma-sprayed HA coatings is difficult. However, partial porosity control is possible with plasma-spraying variables such as powder size, plasma gas composition, powder injection mode, and spray distance, etc. [15].

One of the other quality characteristic of HA coatings is crystallinity. According to the ISO 13779-2 standard, the crystallinity of HA coatings in medical applications should be at least 45%. Crystallinity is directly related to the decomposition that occurs in HA feedstock during the plasma-spraying process. Due to the high plasma enthalpy, when HA particles pass through the plasma flame and reach the substrate, they decompose due to overheating. Thermal decomposition products include of tricalcium phosphate (TCP), tetracalcium phosphate (TTCP), and calcium oxide, as well as the dehydroxylation products oxyhydroxylapatite and / or oxyapatite. The high percentage of decomposed phases reduces the in vivo lifetime of HA coatings. Therefore, high-crystallinity coatings are undesirable. Because high-crystallinity HA coatings are very stable when pH values > 4.5, showing essentially bioinert behaviour, by optimizing the plasma-spray parameters, plasma enthalpy is changed, and thermal decomposition and crystallinity can be controlled. Quality of HA coatings is quite sensitive to the process parameter optimization since unsuitable parameters can decrease the adhesive strength of HA coatings. In addition, to prevent thermal decomposition of HA, researchers have proposed building a bond layer as the HA-substrate interface and incorporating particles into bioceramic layer. Bond coating and particle reinforcement application also have a strong effect on the mechanical properties of HA coatings. To improve the mechanical properties of HA coatings, the researchers investigated the composite and bi-layer coating structure. For plasma-sprayed HA coating, TiO2, Ti, Yttria Stabilized Zirconia (YSZ), and ZrO2 have shown to enhance the mechanical properties of composite coatings in different ratios. In addition, a double-layer coating design with

intermediate layers such as Ti, TiO2, and YSZ has been found to enhance the adhesion strength of the HA coatings. Improvements in corrosion resistance have also occurred [15]. In some implant applications, the implants may be subjected to stresses such as tensile and compressive loads, depending on the shape and position of the bone or implant. In these cases, the coatings lose their mechanical stability and
damage to the coating-implant interface. To avoid this situation, an interface coating with better mechanical properties and elongation tolerance is suggested [17].

For high-porosity coatings deposited on the substrate that has poor corrosion resistance, such as magnesium, the body fluid can leak from the porosities and come into contact with the substrate implant. Corrosion damage to the substrate-coating interface may occur. It has been stated that the use of a high corrosion resistance and biocompatible bond layer prevents the release of ions from substrate implants to the body environment. Thus, the corrosion resistance of the substrate-coating interface is increased [18]. In general, researchers selected YSZ to reinforce HA coating. However, changes in the physical and chemical properties of the coating are unknown as a result of TiSZ into HA coatings. In addition, the presence of Ti ions in reinforcement material is important for biomaterials.

The main purpose of this study is to investigate the effect of TiSZ addition and Ti interlayer on the mechanical properties and corrosion behaviour of plasma-sprayed HA bioceramic coatings on magnesium substrate.

2. Experimental

2.1 Coating Fabrication

A magnesium plate was used as the substrate with a square shape of 1 cm$^2$ and thickness of 2.5 mm. The analysis of energy dispersive spectrometer (EDS) results taken from two different points on the Mg substrate are shown in Table 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.

After the prefabrication process, substrates were fastened in a turntable. Metco 4010 Titanium powder was sprayed using the HVOF method for the double-layer coatings. A DJ2600 HVOF gun and 4MP powder feeder unit were used for spraying. The HVOF operation parameters are presented in Table 2.

Commercially available HA (Particle size:+25-40) and Metco 143 TiSZ (ZrO2 18TiO2 10Y2O3, Particle size: -75 +5) powder were used for bioceramic coating deposition. Fig. 1 shows scanning electron microscopy (SEM) images of the powders. HA powder is spherical, while Ti and TiSZ powders have angular geometry. HA and 10%wt TiSZ powders were added in a plastic bottle and then mixed using Turbula for 4 h.

Bioceramic coatings were produced by atmospheric plasma spray (APS) using a Sulzer Metco 9MB plasma spray gun. The gun nozzle is a commercial 730C, and the powder injection angle was placed perpendicular to the plasma flame. The process parameters of the plasma spray are listed in Table 3.

2.2 Microstructural Characterization
The microstructure, morphology, and chemical composition of the powders and coatings were examined by field emission electron microscopy (JEOL JSM 7000F), which is equipped with an energy dispersive spectrometer. X-ray diffraction (XRD) with CuKα radiation (Rigaku Miniflex) was used to investigate the crystalline structure of the powders and coatings.

2.3 Rockwell-C Adhesion Test

The Daimler-Benz Rockwell-C adhesion test of bioceramic coatings was performed by applying an indentation of 980 N load. After indentation, the sample surfaces were examined by SEM and the adhesion of the coatings according to the VDI 3198 standard was evaluated.

Fig. 2 illustrates the types of shapes of the imprint damage [20].

2.4 Scratch tests

Scratch tests were performed using a standard 100 μm Rockwell-C diamond indenter, creating scratch marks of 8 mm in an incremental load range of 0.05–30 N. During the scratch testing, each coating sample had a drawing speed of 8 mm/min and a loading speed of 30 N/min. Two scratches were formed on each coating surface. Following testing, graphics were drawn on the acoustic emission-force axes, and the scratch lines were examined with an SEM and an optic microscope.

2.5 Electrochemical Corrosion Test

Before starting the electrochemical experiment, the surfaces of specimens were respectively cleaned in acetone, ethyl alcohol, and double-distilled water for 15 min. in an ultrasonic bath at 30°C, followed by drying at 40°C for 1 h in an incubator.

For corrosion experiments, Gamry reference 600 potentiostat/galvanostat and Echem Analyst software were employed to collect data from specimens. Uncoated and coated magnesium specimens were held in a simulated body uid (SBF) solution for 1 h at 37°C to provide solution stability. The current potential diagrams were obtained at the end of the corrosion tests. Corrosion current (Icorr), corrosion rate, polarization resistance, and corrosion potential (Ecorr) values were determined from the current density-potential curves. The corrosion current density (icorr) was then calculated by dividing the corrosion current by the surface area.

3. Results And Discussion

3.1 Microstructural Characterization

Cross-sectional SEM images of single- (SL) and double-layer (DLC) coatings can be seen in Fig. 3. All coatings have traditional microstructure of HA coatings produced by plasma spray. The porosities are clearly seen in the bioceramic coating. EDS analysis taken from the cross-section of coatings shows that the dark regions represent HA and the light regions represent TiSZ regions for TiSZ-reinforced coatings.
TiSZ particles were randomly distributed in HA. The thickness of single-layer bioceramic coatings (Fig. 3 a, b) was approximately 85–100 µm. A titanium layer of about 10–20 µm thickness and 100–120 µm thickness bioceramic layer for the double-layer coatings (Fig. 3 c, d) were obtained. There is continuous adhesion between the Mg substrate and the Ti layers for all coatings. The porosity level of the bioceramic layers was measured at approximately 5%, according to image analysis made by ImageJ software. The TiSZ addition in the bioceramic top coat did not substantially affect by the porosity level.

The high-magnification, cross-sectional SEM images of the bioceramic top coats are illustrated in Fig. 3. A typical, plasma-sprayed hydroxyapatite lamellar structure can be seen in the cross-section microstructure. The lamellar structure formation in plasma-sprayed coatings is explained by two mechanisms, deformation and solidification. When the semi-melted particles in the plasma hit the substrate material, the spherical semi-melted particles are transformed into a cylindrical shape, and the cylindrical splats expand radially. This deformation is affected by many parameters, such as the feedstock melting point, particle size and density, and type of substrate material. In the second stage, the semi-melted splats start to solidify rapidly. This solidification first takes place at the splat–substrate interface and, thus, provides mechanical bonding. Then, the sprayed semi-melted particles accumulate and wet each other to form the coating layer [21]. Some semi-molten HA and TiSZ splats can clearly be seen in a high-magnification SEM image of the HA+10%TiSZ layer. HA coatings have a more regular microstructure than TiSZ-reinforced coatings due to the different behaviours of pure and composite powders during splat-plates accumulation. Depending on the melting points and physical properties of the particles, they may melt to different extent in plasma; thus, a different microstructure may occur. The HA powder used in this study has a melting point of 1570°C [15], while TiSZ has a melting point of 2535°C. In this case, HA particles are transform to the semi-melted form in the plasma jet faster and more easily than TiSZ particles. A detailed SEM image of the bioceramic layers shows that the white TiSZ regions have a thicker splat shape, while the dark HA regions have a thin splat shape. TiSZ particles have a lower melting extent than HA in the plasma jet. Furthermore, HA splats did not wet the TiSZ splats sufficiently. The volume shrinkage of the splats during rapid solidification also caused microporosities and intersplat cracking [22].

The SEM image of the pure HA and TiSZ reinforced HA bioceramic coating surface is shown in Fig. 4. They have a porous and micro-cracked surface morphology. No spherical or semi-molten particles were encountered on the surface of the coating. The dark features represents HA, while the light features represents TiSZ splats in the TiSZ-reinforced HA coatings. The table in Fig. 4 shows the results of EDS analysis taken at the TiSZ-reinforced coating surface. The dark regions contain hydroxyapatite-forming elements such as Ca, P, O, and K. The presence of K in the HA structure has been explained as an impurity in previous studies. Some reagents such as potassium sulphate and potassium phosphate are used to synthesize synthetic HA, and some residual K element remained in the structure [23-25]. The Ca / P ratio is 1.665. These elements are also found in compounds such as tricalcium phosphate and tetracalcium phosphate. HA is distinguished by the Ca / P ratio from these compounds. The Ca / P ratio of HA was reported to be 1.67, Ca / P = 1.5 for tricalcium phosphate and 2 for tetracalcium phosphate [15].
Fig. 5 shows the XRD pattern of titanium powder (a) and as HVOF sprayed coatings (b). Several low-intensity titanium oxide peaks can be identified, unlike in the Ti powder XRD pattern. During HVOF spraying, the particles were heated to temperatures up to 2500°C. The in-flight particles reacted with oxygen in the atmosphere while cooling on the air or substrate. This resulted in the formation of some oxide such as TiO and Ti2O3 in the coating [26].

The XRD pattern of HA powder is shown in Fig. 6 a). As seen in the diffractogram, HA powder consists of HA- Ca5(PO4)3(OH), α-TCP-Ca3(PO4)2 and TTCP-Ca4O(PO4)2 phases. Fig. 6 b) shows the XRD pattern of HA bioceramic coatings. After the plasma spraying, the peak intensity of the coating was reduced compared to the HA powder. It is understood that the crystalline phase in the HA structure transforms into the amorphous phase [15, 27]. Previous studies have reported that decomposition occurs during plasma spraying of HA powder due to high plasma enthalpy and solidification on the substrate [15]. As a result of this decomposition, new phases such as α-TCP, β-TCP, TTCP and CaO are formed.

According to the XRD patterns of HA coatings reinforced by TiSZ in Fig. 3 d), it is determined that the phase structure consists of HA, α-TCP, TTCP and tetragonal zirconia. However, since the α-TCP peak in the $2\theta = 31–32^\circ$ range coincided with the tetragonal zirconia peak, the intensity of the peaks in this position increased compared to the XRD pattern of pure HA [28].

3.2 Rockwell-C Adhesion Test Results

Fig. 7 shows the SEM images of indentation zones after Rockwell-C adhesion tests. The SEM images were evaluated according to the VDI 3198 standard. In Fig. 7 a) and b), it can be seen that the damage caused by indentation is in the unacceptable classes of HF5 and HF6. There are many delamination around the indentation zone in both coatings. The Ti bond layer for the pure HA coating has no significant effect on the Rockwell-C adhesion behaviour of the HA coatings, and the interfacial adhesion strength of pure HA coatings is poor.

The SEM images of the Rockwell-C indentation zone of the single- and double-layer HA+10 wt%TiSZ coatings are shown in Fig. 7 c) and d). The damages are in the HF3 class for the single layer coating and in the HF4 class for the double layer coating. The coating around the indentation zone did not spall due to the stresses, and very little deformation has occurred.

When the Rockwell-C adhesion test results were evaluated generally, it was found that the adhesion of TiSZ-reinforced HA coatings were in an acceptable class, except for the single and double-layer HA. The presence of a Ti interlayer in the TiSZ-reinforced HA coatings improved the Rockwell-C adhesion behaviour of coatings [29].

To improve the mechanical properties of bioceramic HA coatings, researchers have generally attempted YSZ reinforcement. Bang-Yen Chou et al. [30] produced 10%wt 8YSZ / HA composite coatings on Ti6Al4V substrates as a single layer and double layer with 8YSZ bond coat by plasma spraying. The bonding strength of the coatings was measured according to the ASTM C633-79 standard. A composite and
double-layer coating structure increased adhesion strength. With the 8YSZ additive to plasma-sprayed HA, the porosity ratio of the coatings has decreased and cohesive failures have been reduced. A double-layer and composite coating design in the study by Chou et al. showed an effect similar to that of the present study.

Lei Fu et al. [31] produced 10%, 30%, and 50%wt YSZ-reinforced HA coatings with plasma spraying. They stated that the elastic modulus and fracture toughness of the coatings improved with increasing amounts of YSZ. They reported that the reason for this improvement was the unmelted, large-volume YSZ splat microstructure compared to the HA splats dispersed in the composite coating structure.

As previously discussed in relation to coating microstructures, the porosity ratios for pure and reinforced HA bioceramic coatings are very similar. But when detailed SEM pictures are examined, pure HA has a more regular splat morphology than TiSZ-reinforced HA.

Microcracks are clearly seen on HA-TiSZ splat interfaces. These cracks or gaps can restrict the crack propagation that progresses from the other areas. In addition, the dispersion of poorly melted high volumes of TiSZ splats in the HA matrix improved the fracture toughness and elastic modulus of the bioceramic coatings.

### 3.3 Scratch test results of coatings

Fig. 8 shows the acoustic emission-force graphics, optical microscope and SEM image of scratch lines. In the optical microscope images, it is observed that there is no adhesive damage for any scratch lines except for HA + 10%wt TiSZ scratch line 2 (see Fig. 8 c). In the second scratch line in the HA + 10%wt TiSZ coating, when the load approached 25N, adhesive damage occurred and the coating was spalled. However, considering that the coating microstructures contain defects such as porosities, this damage can be considered to have low reliability for determining the exact critical force for the adhesion strength of the coatings. When acoustic emission-force graphics are examined, the fewest and lowest-intensity peaks occurred in single-layer coatings. In double-layer coatings, the acoustic emission peaks are more numerous and more severe. Since there is no adhesive damage on the coatings, the acoustic emission peaks represent the formation of cracks cohesive in the bioceramic layer. Cohesive failure formation is closely related to several physical properties of coatings such as hardness, elastic modulus, fracture toughness, and surface roughness, and these have very complex relationships. As discussed previously, the YSZ reinforcement for HA coatings improves the mechanical properties of the coatings such as elastic modulus, fracture toughness and hardness. According to this theory, fewer and lower acoustic emission peak is expected due to less crack formation in the TiSZ-reinforced HA coatings. However, an improvement similar to that of Rockwell-C adhesion tests was not observed in the mechanical properties of the bioceramic layer due to TiSZ reinforcement. The reasons can be explained as follows: the distribution of TiSZ splats in the HA-coating microstructure impairs mechanical homogeneity, and TiSZ splat zones (55 HRC) are harder than the HA (43 HRC) matrix [32]. This ensures that the indenter progresses by making acute up-and-down movements in the coating [33]. In addition,
poor bonding between HA and TiSZ splats and intersplat cracks promote crack formation during scratch tests. This causes further crack formation and acoustic emission peaks [34, 35]. This statement applies to single-layer bioceramic coatings and is insufficient for the double-layer coating system. In double-layer coatings, surface roughness is effective in scratch behaviour. In the surface-roughness measurements, it was determined that double-layer coatings (6.2 µm) were rougher than single-layer coatings (4.8 µm). A high level of surface roughness increased the friction coefficient, and crack formation started as cohesive damage in the coatings from low forces. As the force increased, the indenter progressed by creating more cracks due to the debris it added to the front. Thus, more acoustic emission peaks occurred in double-layer coatings [35]. In addition, scratch lines were examined with SEM to better define the acoustic emission regime of coatings. According to SEM examinations, it was observed that more tensile cracks were formed in the double-layer coating than in the single-layer coatings. This is related to the surface roughness of the coatings. In summary, the cohesion resistance to shear stresses such as scratches is higher in single-layer coatings than in double-layer coatings.

### 3.4 Electrochemical corrosion test results

Fig. 9 shows the Tafel curves obtained from the measured corrosion variables. It can be seen that the double-layer coatings have less Icorr corrosion current density changes when compared with the single layers. In addition, the Icorr corrosion current density for the uncoated Mg alloy moved in a strongly negative direction. The intensity of this action was significantly reduced by the production of coating on the substrate. For the double-layer coatings in the anodic zone, the change in corrosion current density is less than that in the cathodic region. In the single-layer coatings, the change in corrosion current density showed close and balanced changes between the anodic and cathodic regions.

Table 4 shows the values of corrosion variables of Mg substrates and coatings. The corrosion potential Ecorr value is low and the corrosion current density is very high for uncoated Mg. Previous studies about Mg alloy for biomedical application reported that the corrosion rate of uncoated Mg is high in the SBF solution. However, the corrosion rate was significantly reduced for the bare Mg substrate after coating. While the corrosion rate for uncoated Mg was 11.61 mpy, these values ranged from 1.311 to 1.620 for single-layer HA, and HA+10%TiSZ reinforces coatings respectively. In addition, the Icorr corrosion current density showed a significant decrease in the single-layer coatings compared to the uncoated substrate. The polarization resistance of the Rp value is quite low compared to the coatings for Mg substrate. In single-layer coatings, the TiSZ additive has a negative effect on the corrosion behaviour of bioceramic HA-based coatings. The lowest corrosion rate was obtained in the pure HA coating for the single- and double-layer designs. The presence of a titanium intermediate layer reduced the corrosion rate for the pure HA [18]. Conversely, the production of double-layer TiSZ reinforced the HA-Ti coatings, which caused an increase in corrosion rate and negatively affected the corrosion behaviour of the coatings.

When the surface SEM images of the coatings in Fig. 4 are examined, it is clearly seen that the TiSZ-reinforced HA has a higher-porosity surface structure than pure HA. It is known that the corrosion
resistance of low-porosity surfaces is higher. Therefore, the corrosion resistance of pure HA in single-layer and double-layer coatings is higher than that of TiSZ-reinforced HA coatings [36]. Yugeswaran et al. [32] produced HA and HA + 10, 20, 30%wt YSZ-reinforced coatings using a gas tunnel type plasma spray. As a result of electrochemical corrosion tests, YSZ reinforced HA coating, resulting in a significant reduction in corrosion rate. This is related to the decrease of the porosity percentage of HA coatings from the cross-section as a result of YSZ reinforce. In this study, the porosity measurements made from the cross-section are close to each other for all coatings. Reinforcing HA with TiSZ when the porosity effect was neglected had a negative effect on corrosion resistance. Singh et al. [27] produced HA and 10wt 80% Al2O3-20TiO2 composited coatings by plasma spraying. They reported that pure HA has higher corrosion resistance despite the decrease in the porosity rate due to the reinforcement of HA according to electrochemical corrosion tests. Icorr values of the coatings were calculated as 1.53 and 1.59. These values are close to those in the present study.

Fig. 6 c) shows the XRD graph of HA coatings after electrochemical corrosion testing. Comparing the XRD pattern before and after electrochemical corrosion testing, both XRD patterns are almost the same. However, an increase in HA peak heights between $2\theta = 32–35^\circ$ is observed. Fig. 6 e) shows the XRD graph after the electrochemical corrosion test of TiSZ-supported coating. Comparing XRD graph before and after corrosion, it is seen that peak heights increase after corrosion. The amorphous phase dissolved and coating crystallinity increased during the corrosion tests. Previous studies have reported that the amorphous phase is more easily dissolved in SBF than the crystalline phases [36, 37]. The crystalline percentage of coatings increased with the dissolution of the amorphous phase. The same mechanism can be noted for pure HA coatings.

### 4. Conclusion

In this study, bioceramic pure HA coatings and 10%wt TiSZ-reinforced HA coatings were successfully coated on the magnesium substrate as a single layer and double layer with the Ti bond layer that is produced by HVOF. According to the characterization results and discussions in previous contents the following conclusions can be drawn:

- The adhesion strength of plasma-sprayed HA bioceramic coatings for SL and DLC designs is increased with the addition of TiSZ. However, the cohesion behaviour of the HA-based bioceramic layer was negatively affected for the SL design. The TiSZ addition for SL and DLC coatings reduced the corrosion resistance of coatings.

- The presence of the Ti bond layer is ineffective for the adhesion and cohesion behaviours of HA bioceramic coatings. However, it increased the corrosion resistance of bioceramic coatings.

- Long-term immersion tests are needed to test Ti bond layer stability for Mg-based implant materials. HVOF process parameters can be optimized to eliminate or minimize oxide phases in the bond layer.
Declaration

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Tables

Table 1. Chemical composition of Mg substrates.

|       | C   | O   | Mg   | Mn   | Total  |
|-------|-----|-----|------|------|--------|
| Substrates | 4.8 | 3.42| 91.78| 0.78 | 100.00 |
|        | 2.48| 5.40| 91.40| 0.72 | 100.00 |

Table 2. HVOF process parameters.

| HVOF                          | Titanium |
|-------------------------------|----------|
| Powder feed rate (gr/dk)      | 10       |
| Spray Distance [19]           | 250      |
| Propane flow rate (Scfh)      | 40       |
| Oxygen flow rate (Scfh)       | 24       |
| Air flow rate (Scfh)          | 50       |
| Turntable speed (Hz)          | 50       |
| Spray angle (°)               | 90       |

Table 3. Process parameters for plasma spray.

| Plasma Spray                  | HA/TiSZ  |
|-------------------------------|----------|
| Current (A)                   | 400      |
| Primary gas flow rate, Ar (scfh)| 90    |
| Secondary gas flow rate, H2 (scfh)| 15    |
| Carrier gas flow rate, Ar (scfh)| 13.5  |
| Spray distance [19]           | 75       |
| Turntable speed (Hz)          | 40       |
Table 4. Electrochemical test result of coatings.

| Solution      | Icorr. (µA) | Eco. (V) | Corrosion Rate (mpy) | Rp value (kΩ) |
|---------------|-------------|----------|-----------------------|---------------|
| Mg Unc.       | 21,90       | -1,46    | 11,61                 | 0,901         |
| SB Sub.       | 1,46        | -1,32    | 1,31                  | 17,21         |
| Single        | HA-10%TiSZ  | 1,80     | -1,31                 | 1,620         | 11,93         |
| Double        | HA          | 1,21     | -1,01                 | 1,098         | 25,92         |

Figures

Figure 1

SEM image of powders: a) HA, b) Ti, c) TiSZ.
Figure 1

SEM image of powders: a) HA, b) Ti, c) TiSZ.

Figure 2

The principle of the VDI 3198 indentation test.
Figure 2

The principle of the VDI 3198 indentation test.

Figure 3

Cross-sectional SEM image of coatings: a) HA, b) HA+10%TiSZ, c) HA-Ti, d) HA+10%TiSZ-Ti.
Figure 3

Cross-sectional SEM image of coatings: a) HA, b) HA+10%TiSZ, c) HA-Ti, d) HA+10%TiSZ-Ti.
### Figure 4

SEM image and EDS analysis results of bioceramic coating surface, a) HA, b) HA+10%TiSZ.

| Element | Atomic Conc. | Weight Cons. | Oxyde Sym. | Stocio. Conc. | Atomic Conc. | Weight Cons. | Oxyde Sym. | Stocio. Conc. |
|---------|--------------|--------------|------------|---------------|--------------|--------------|------------|---------------|
| O       | 75.60        | 56.78        | Ca         | 58.26         | O            | 59.93        | 27.28      |               |
| Ca      | 14.22        | 26.74        | Ca         |               | Zr           | 14.89        | 38.64      | 37.15         |
| P       | 8.54         | 12.42        | P          | 35.01         | Ca           | 9.50         | 10.84      | 23.72         |
| K       | 1.15         | 2.10         | K          | 4.69          | Ti           | 9.21         | 12.55      | 22.99         |
|         |              |              |            |               | K            | 4.00         | 4.45       | 9.98          |
|         |              |              |            |               | Y            | 2.47         | 6.25       | 6.16          |
Figure 4

SEM image and EDS analysis results of bioceramic coating surface, a) HA, b) HA+10%TiSZ.
Figure 5

XRD patterns of a) Ti powder, and b) HVOF Ti coating.
Figure 5

XRD patterns of a) Ti powder, and b) HVOF Ti coating.
Figure 6

XRD patterns of coatings, a) HA powder, b) HA coating, c) HA coating after corrosion, d) HA+10%wtTiSZ coating, e) HA+10%wtTiSZ coating after corrosion.
Figure 7

SEM images of Rockwell-C indentation, a) HA, b) HA-Ti, c) HA+10%TiSZ, d) HA+10%TiSZ-Ti.
Figure 7

SEM images of Rockwell-C indentation, a) HA, b) HA-Ti, c) HA+10%TiSZ, d) HA+10%TiSZ-Ti.
Figure 8

Acoustic emission-force graphics, optical microscope and SEM images of scratch line of coatings, a) HA, b) HA-Ti, c) HA+10%wt TiSZ, d) HA+10%wt TiSZ-Ti.
Figure 9

Tafel plots of Mg substrate single layer (SL) and double layer (DLC) coatings.
Figure 9

Tafel plots of Mg substrate single layer (SL) and double layer (DLC) coatings.