Applications of Thermal Spray Coating in Artificial Knee Joints

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Abstract: With remarkable medical advances, aging population makes the artificial knee joint replacement increasingly popular, and the quality of total knee replacement depends on materials selection and the application of surface coating. Titanium alloys have been widely used as artificial knee joint material due to their specific properties such as low density, toxicity and excellent corrosion resistance and biocompatibility. Thermal spray coating technology is used worldwide in many industrial applications, but the application of thermal spray biocompatible coatings on the titanium alloy surface in the biomedical field as to improve the knee's functions is a relatively new area. The purpose of this study was to make a comprehensive overview of applications and characterizations of titanium alloy surface coating in artificial knee joint by thermal spray coating technology.
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Keywords Thermal spray coating; Artificial knee joint; Titanium alloy

1. Introduction

With medical advances, life expectancy gradually extends. As people become older, the human bones and joints wear badly due to long-term use and deterioration. Then it leads to pain or malfunction of joints. When joint disease becomes severe, artificial joint replacement surgery can significantly relieve pain and improve joint function. Knee joints are the largest and most important joints, which are vulnerable to various injuries and diseases. Currently there are around 20,000 cases per year for the artificial knee joint replacement surgery in Taiwan, and this surgery is fairly common in orthopedic surgery [1-3]. Knee structure is mainly composed of the femur, tibia, patella and meniscus formed and fixed by the external muscles and ligaments. Typical components commonly used in artificial knee joint contain the femoral components, tibial components, patella and tibial bearing component as shown in Figure 1[4]. Existing artificial knee joint biomedical materials are metals, ceramics, polymers and composite materials. Because the metallic materials have excellent mechanical properties, easy processing and stability, they have been widely used in artificial joints [5-10]. The selection criteria for biomedical metallic material are: the minimum biological response in the body and to meet the basic functional requirements of the replacement and repair tissues. Owing to the mechanics and the common needs of the body environment, three types of metallic materials (stainless steel, cobalt alloys and titanium alloys) are mainly used for the artificial knee joint. Among them, titanium alloys are the preferred medical materials because of density as close to human bones, low modulus, corrosion resistance and biocompatibility better than stainless steel and cobalt alloy [11, 12].

Thermal spray technology encompasses a group of coating processes that provide functional surfaces to protect or improve the performance of a substrate or component. Many types and forms of materials can be thermal sprayed—which is why thermal spray is used worldwide to provide protection from corrosion, wear, and heat; to restore and repair components; and for a variety of other applications [13, 14]. Compared with other industrial applications, biomedical coating is a relatively new class of applications for thermal spray coating [13-16]. Thermal spray processes are grouped into three major categories: flame spray, electrical arc spray, and plasma arc spray. These energies sources are used to heat the coating material (in powder, wire, or rod form) to a molten and semi-molten state. The resultant heated particles are accelerated and propelled towards a prepared surface by either process gases or atomization jets.

Titanium alloys with excellent mechanical and biological properties have been proven to be effective in clinical medical application. In order to improve the biological activity, wear resistance and corrosion resistance of titanium alloy, the implementation of its surface modification becomes quite important [17, 18]. The types of coating applied in the artificial knee joint are usually biological coatings. These biological coatings mainly include aluminum oxide (Al_2O_3), zirconia (ZrO_2) and Hydroxyapatite (HA). The purpose of this study was to make a comprehensive overview of applications and characterizations of titanium alloy surface coating in artificial knee joint by thermal spray coating technology, in order to understand and master the titanium surface modification technology and related mechanisms.

Figure 1 The components of an artificial knee joint.

2. Experimental Procedures

2.1 Experimental Materials

The materials used in this study were bars and plates of titanium alloys (Ti-6Al-4V). The bars were mainly used for bond strength test, and the plates were used in many tests. They were used for the wear test, observing metallographic microstructure, hardness and other tests. The properties of titanium alloy are shown in Table 1, the sample size of the bar isφ25.4mm × 30mm and the plate is 75 × 25 × 35mm, as shown in Figure 2 (a) and 3 (b).

Table 1 The material properties of titanium alloy tested.

Chemical composition	Al	V	Fe	C	N	H	O	Ti
	5.5-6.75	3.5-4.5	≤0.20	≤0.08	≤0.05	≤0.015	≤0.020	Remainder
Mechanical Properties	Tensile Strengh(MPa)		Yield Strengh(MPa)		Elongation(%)		Bending test	Hardness(HRC)
	≥895		≥825		≥10		≥25°	34°±2

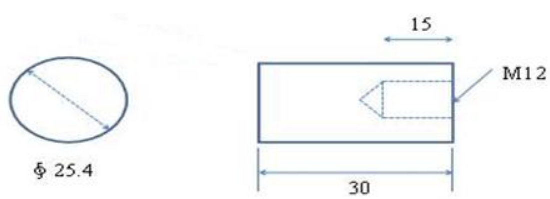

Figure 2(a) Schematic diagram of sample size for the bond test (ASTM C633).

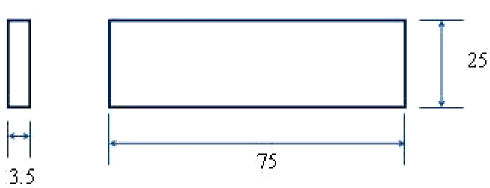

Figure 2(b) Schematic diagram of sample size for the wear test (ASTM G65).

2.2 Thermal Spray Coating Technology

The atmospheric plasma spray (APS) equipment made by Sulzer Metro Company (Spray Gun Type: 9MB) was used in this study. Plasma temperatures in the powder heating region range from 6000 to 15,000℃, significantly above the melting point of any known material. Three kinds of powder materials such as alumina (Al_2O_3), zirconia (ZrO_2) and hydroxyapatite (HA) are melted respectively, and then molten particles were guided through by air to form a coating on the substrate, as shown in Figure 3. Al_2O_3 and ZrO_2 ceramic materials are biologically inert, while the HA is a bioactive ceramic material. Hydroxyapatite (HA) is calcium phosphate ceramic $[Ca_{10}(PO_4)_6(OH)_2]$ that exhibits strong activity for joining to bone tissue.

The thermal spray process conditions of the three coating materials were shown in Table 2. Table 2 shows the important parameters affecting the quality of the coating, which includes inert gas composition, current, voltage, powder feeding rate, spraying distance and etc. HA powder was used in the inert gases of argon and helium, which is different from the Al_2O_3 and ZrO_2 used in the argon and hydrogen gas mixture. Before coating, the substrate surfaces were cleaned, degreased, and roughened in order to improve the bonding strength.

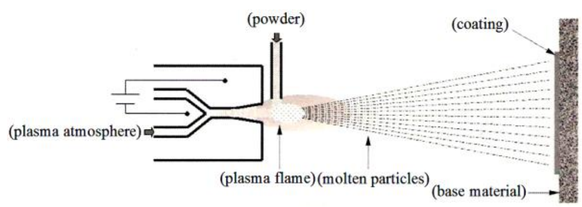

Figure 3 Schematic diagram of thermal spray coating [13].

Table 2 Thermal spray parameters for HA、Al_2O_3、ZrO_2 powders.

Hydroxyapatite (HA)									
Parameters	Argon (l/min)	Helium (l/min)	Current A	Voltage V	Powder rate (g/min)	Spray distance (mm)	Surface speed (75m/min)	Traverse speed (8mm)	Cooling
Setting	41	60	700	52	30	115	75	8	yes
Al_2O_3									
Parameters	Argon (l/min)	Hydrogen (l/min)	Current A	Voltage V	Powder rate (g/min)	Spray distance (mm)	Surface speed (75m/min)	Traverse speed (8mm)	Cooling
Setting	41	14	600	72	35	110	75	8	yes
ZrO_2									
Parameters	Argon (l/min)	Hydrogen (l/min)	Current A	Voltage V	Powder rate (g/min)	Spray distance (mm)	Surface speed (75m/min)	Traverse speed (8mm)	Cooling
Setting	41	9	600	68	28	120	75	8	yes

2.3 Characterization of Surface Coating

The surface coating quality of three kinds of coating materials (Al_2O_3, ZrO_2, HA) on Ti-6Al-4V titanium alloy substrate by plasma thermal spraying was tested and characterized. These tests include coating appearance inspection, surface roughness measurement, coating thickness measurement, bond strength test (ASTM C633), the porosity test, abrasion test (ASTM G65), hardness test and analysis of metallographic microstructure.

3. Results and Discussion

3.1 Coating Appearance Inspection

The initial coating quality information can be obtained by visual inspection of appearance after thermal spray coating. The appearance inspection focuses on the existence of macroscopic defects such as coarse particles, coating spalling, cracks, shadows, or deformation. The results, as shown in Figure 4, showed that there are no coarse particles, coating spalling, cracks and other defects on the coating surface, and the coating layer is smooth, coating color is even without overheating oxidation.

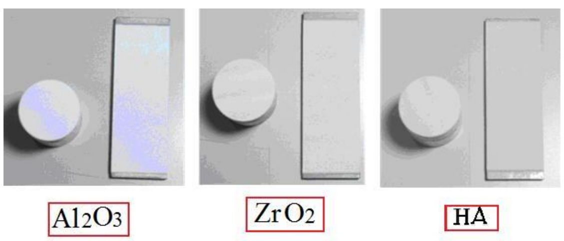

Figure 4 Coating appearance inspection of three kinds of coating materials.

3.2 Surface Roughness Measurement

Surface morphology of the coating can be obtained by surface roughness measurement. The central average roughness (Ra) and the ten-point average roughness (Rz) are commonly used as index of surface roughness. The results indicated that ZrO_2 has the larger surface roughness (Ra, Rz) than Al_2O_3 and HA.

Table 3 Surface roughness measurements of ZrO_2, Al_2O_3 and HA.

Specimen	Ra	Rz
Al_2O_3	5.556μm	43.732μm
HA	7.235μm	54.906μm
ZrO_2	9.973μm	71.223μm

3.3 Coating Thickness Measurement

The results of the coating thickness of three coating materials under the thermal spray process parameters in Table 2 were acquired by the metallographic observation of the specimen and shown in Table 4 and Figure 5 (a) ~ (c).

3.4 Bond Strength Test (ASTM C633)

The main purpose of the test is to understand the adhesion between coating and substrate. The tensile test is commonly used to evaluate the bond strength per ASTM C633 standard method [19]. The schematic of the bond strength test is shown in Figure 6. Bond strength test results showed that HA coating has the lower bond strength (33.2MPa) than Al_2O_3 (47.1MPa) and ZrO_2 (55.9MPa) coating, as shown in Table 5.

Table 4 Coating thickness measurements of three different coating materials under the thermal spray process parameters in Table 2.

Specimen	Thickness (um)
ZrO_2	237~273
Al_2O_3	346~364
HA	246~260

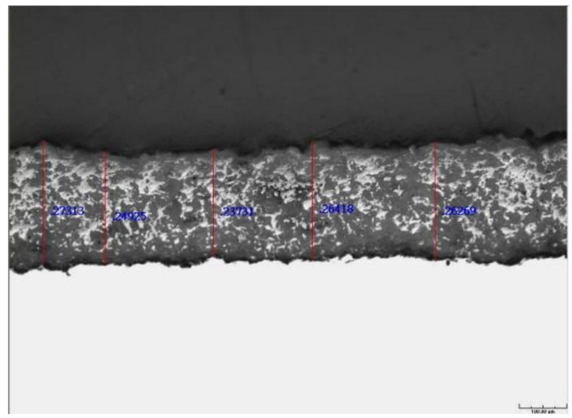

Figure 5(a) ZrO_2 coating, magnification 100X.

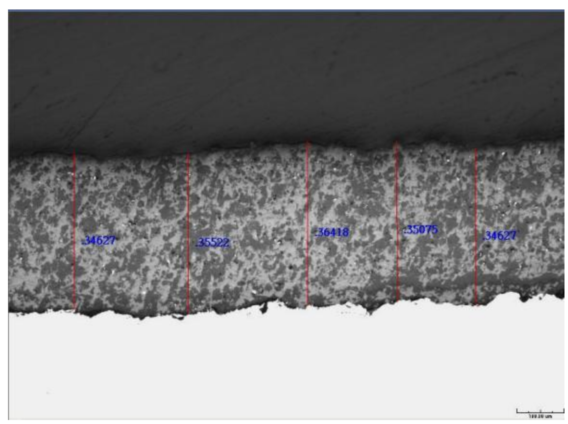

Figure 5(b) Al_2O_3 coating, magnification 100X.

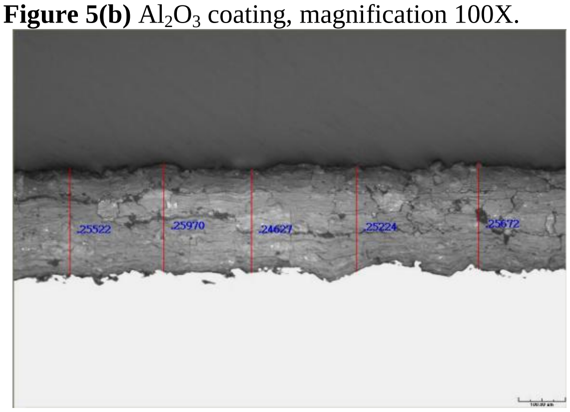

Figure 5(c) HA coating, magnification 100X.

Table 5 Bond strength test results of three different coatings.

Coating type	Bond strength
HA	33.2MPa
Al_2O_3	47.1MPa
ZrO_2	55.9MPa

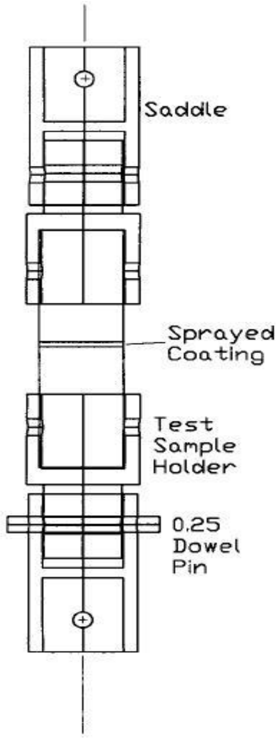

Figure 6 Schematic diagram of bond strength test

3.5 Porosity Test

The specimens (HA , Al_2O_3 , ZrO_2w) were prepared by mounting, grinding and polishing processes and observed randomly the selected three individual locations using an optical microscope, then analyzed by image analysis software. The porosity results were shown in Table 6 and Figure 7 (a) ~ (c). The results showed that porosity of the coating of Zirconia(ZrO_2) and Alumina(Al_2O_3) was less than Hydroxyapatite(HA) coating.

Table 6 Porosity test results of ZrO_2 , Al_2O_3 and HA coatings.

Coating type	Porosity（%）	Mean（%）
ZrO_2	1.17 1.10 1.31	1.19
Al_2O_3	1.55 1.58 2.20	1.54
HA	5.67 5.28 2.87	5.49

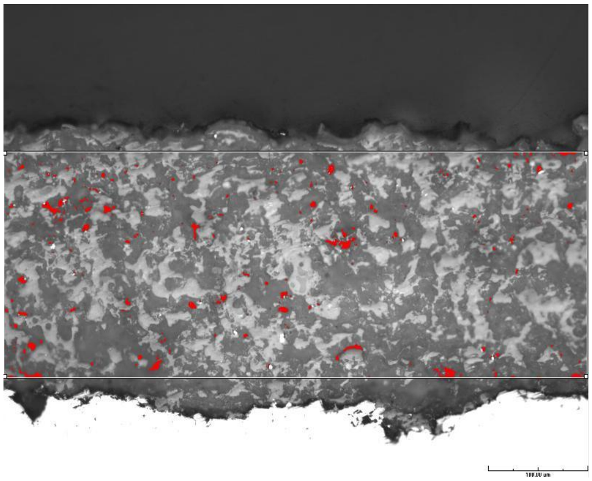

Figure 7(a) The porosity test result of Zirconia (ZrO_2) coating, the red zones are the holes.

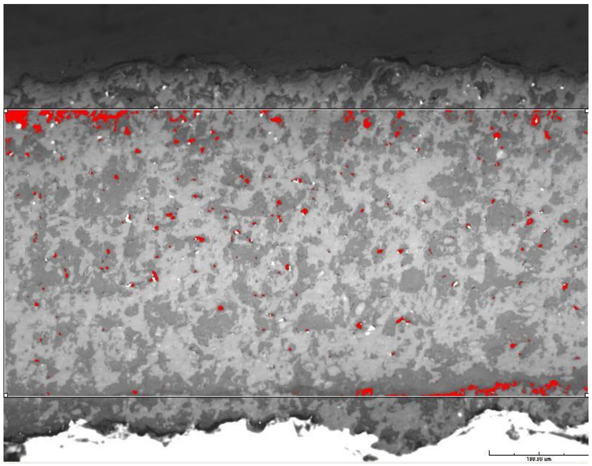

Figure 7(b) The porosity test result of Alumina (Al_2O_3) coating, the red zones are the holes.

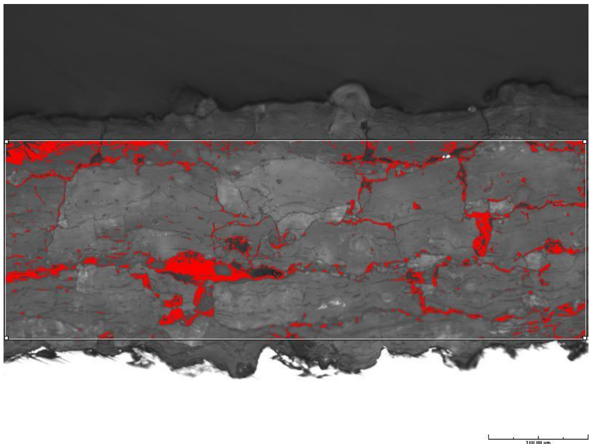

Figure 7(c) The porosity test result of Hydroxyapatite (HA) coating, the red zones are the holes.

3.6 Abrasion Test (ASTM G65)

The abrasion test is based on the ASTM G65 specification [20]. This test is a way of abrasive particle wear with rubber wheels and round quartz. The schematic of the abrasion test was shown in Figure 8. The abrasion test (ASTM G65) results showed that HA has lower volume wear rate than Al_2O_3 and ZrO_2, as shown in Table 7.

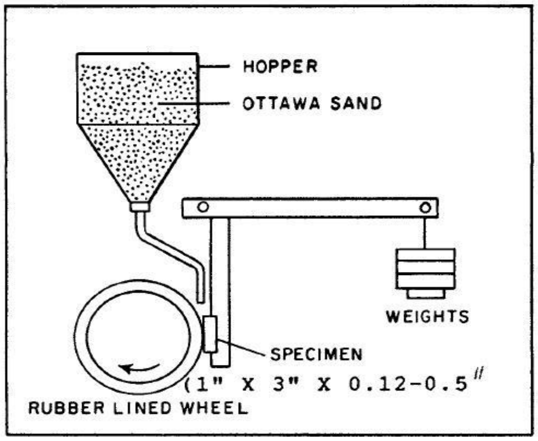

Figure 8 Schematic diagram of abrasive wear test [13].

Table 7 Abrasion test results of three different coating materials.

Specimen	HA (Densit：3.08 g/cm³)	Al_2O_3 (Density：3.3 g/cm³)	ZrO_2 (Density：4.48 g/cm³)
Weight before wear (g)	31.43	31.29	31.49
Weight after wear (g)	31.34	31.17	31.15
Mass loss (g)	0.09	0.12	0.34
Volume Loss (mm³)	29.22	36.36	75.89

$$\text{Volume Loss(mm}^3) = \frac{mass\ loss(g)}{density(^g/_{cm^3})} \times 1000$$

3.7 Hardness Test

The micro-hardness test method (Vickers Hardness) was used to measure the hardness of Ti-6Al-4V substrate and the coating layers (at different locations). The results indicated that the micro-hardness values of ZrO_2, Al_2O_3 and HA are much higher than that of Ti-6Al-4V substrate as shown in Table 8. In addition, the inside hardness of coating is higher than the middle and outer hardness.

Table 8 Micro-hardness test results of three coating materials.

Specimen	Outside	Middle	Inside	Ti substrate
ZrO_2	381	391	412	337
Al_2O_3	407	409	411	332
HA	388	407	396	325

3.8 Metallurgical Microstructure Analysis

The thermal spray coating may result in many defects within the coating because the characteristics of the technology itself or improper process control. Through metallographic microstructure analysis, the quality of the thermal spray coating can be verified. The defects of three different coatings were shown in Table 9 and Figure 9 (a) ~ (g). Table 9 showed that three kinds of coatings are free of cracks, interface contamination, not molten particles, clusters of oxides and strip oxides, but with the phenomenon of layer spalling and interface separation. These results indicated that the adhesive strength between the coating layers and the bond strength between the coating and the substrate are weak. There were not any huge holes found in ZrO_2 and Al_2O_3 coating, however huge holes were found in HA coating (Figure 10 (g)). The existence of a small amount of small holes in the coating is usually normal. However, large holes or high porosity will have an adverse impact on mechanical properties of the coating, such as lower bond strength. The existence of huge holes and high porosity in HA coating can explain why the bond strength of HA coating is lower, as shown in Table 5.

Table 9 Coating defects of three different coating materials.

Specimen	ZrO_2	Al_2O_3	HA
Crack	N	N	N
Coating spalling	Y	Y	Y
Interface contamination	N	N	N
Interface separation	Y	Y	Y
Not molten particles	N	N	N
Huge holes	N	N	Y
Clusters of oxides	N	N	N
Strip oxides	N	N	N

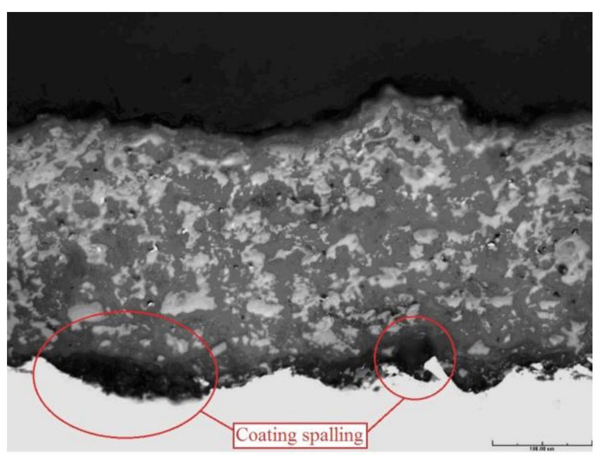

Figure 9(a) ZrO_2 coating, magnification 200X.

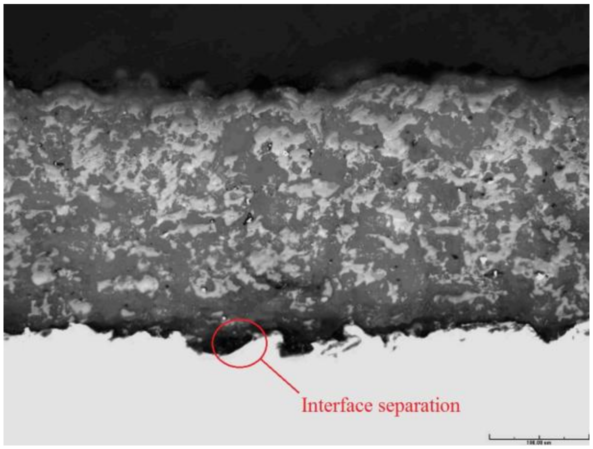

Figure 9(b) ZrO_2 coating, magnification 200X.

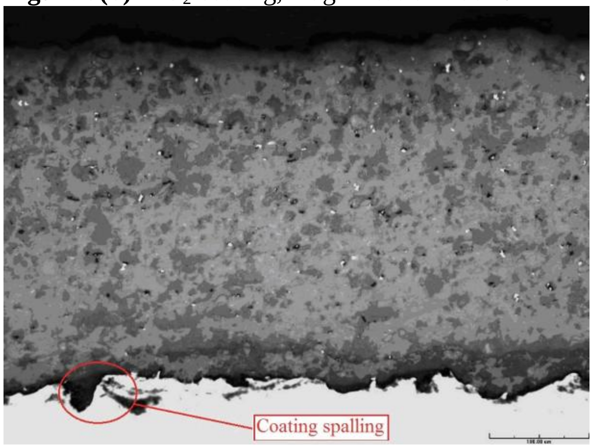

Figure 9(c) Al_2O_3 oxide coating, magnification 200X.

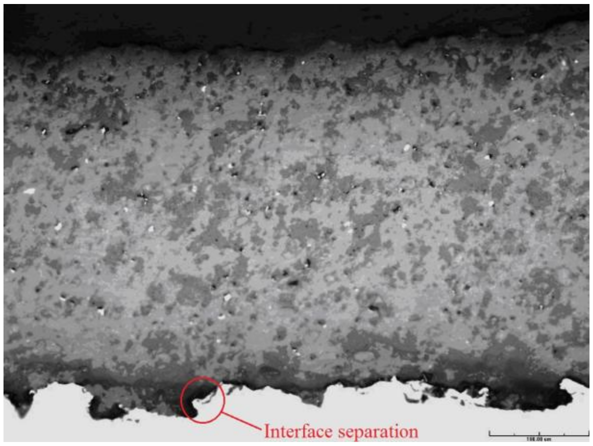

Figure 9(d) Al_2O_3 oxide coating, magnification 200X.

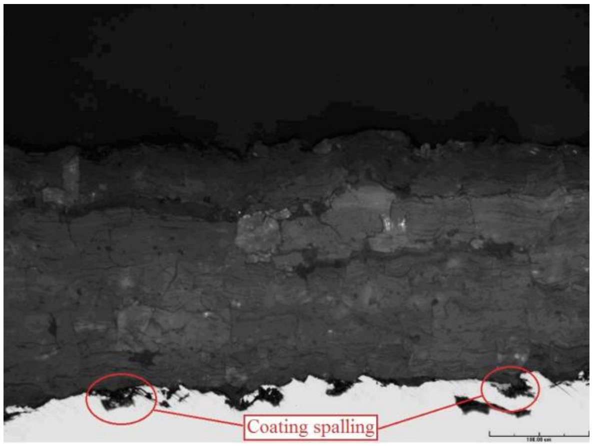

Figure 9(e) HA coating, magnification 200X.

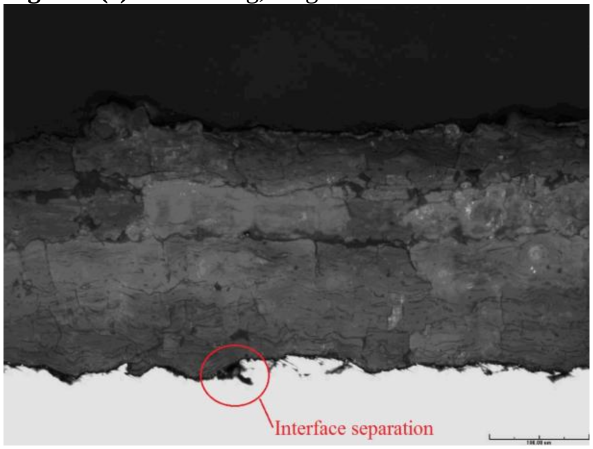

Figure 9(f) Hydroxyapatite coating, magnification 200X.

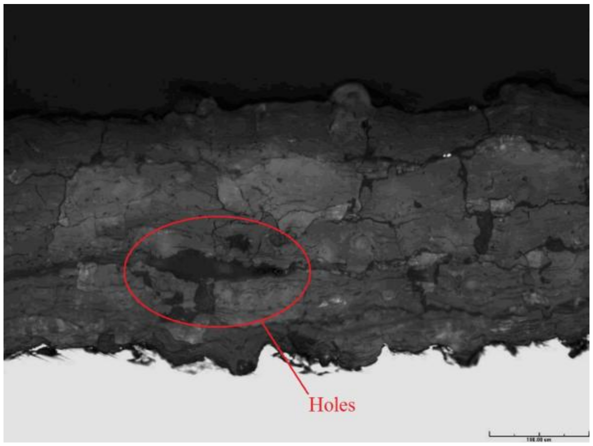

Figure 9(g) Hydroxyapatite coating, magnification 200X.

4. Conclusions

In this study, we have made a concise and comprehensive overview of applications and characterizations of titanium alloy surface coating in artificial knee joint by thermal spray coating technology although the experimental results were preliminary. Due to the different material properties, the process parameters of atmospheric plasma spraying for the three commonly used biological coating materials (Al_2O_3, ZrO_2, HA) were quite different, experimental results displayed the very different characteristics of surface roughness, coating thickness, bond strength, porosity, abrasion, hardness and metallographic microstructure of these three coating materials. In addition, the coating spalling and interface separation were found in Al_2O_3, ZrO_2 and HA coatings from the metallographic microstructure analysis, and there is a problem of higher level of porosity and huge holes in the HA coating. Further studies need to be done to verify the effects of APS process parameters (such as spraying program voltage, current, spraying distance, gas flow and gas composition parameters, feed particle size, feeding rate) and pre-treatment status (cleaning) of the substrate surface on the coating quality.

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