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Effects of Process Parameters on the Coating Properties of APS TiO_2 Bioceramic Coatings

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ABSTRACT

The effects of process parameters on coating formation and coating properties were investigated using a fused and crushed TiO_2 powder by the Taguchi method and $L_9(3^4)$ orthogonal array. The Taguchi analysis was conducted through the results of the coating properties affected strongly by plasma spraying parameters and TiO_2 powder was sprayed on Ti-6Al-4V alloy substrate. The coating properties were characterized by thickness, microhardness, porosity and surface roughness using optical microscopy, image analyzer and surface roughness tester respectively. An observed optimum condition of plasma spraying process could be found for potential use as a bioceramic coating.

Key words : Taguchi analytical method, TiO_2, Plasma spraying, Surface roughness, Porosity, Microhardness

1. Introduction

Plasma spraying of ceramic coatings has become well established as a commercial process over the past 35 years. However, the simplicity of the process, from a practical point of view, has meant considerable empirical development has taken place with relatively little understanding of the basic principles of coating formation. Since coatings are formed by the impact of a stream of particles striking the substrate, the major factors which control the structure of a particular coating are temperature, velocity and size distribution of the incident particles.[1] To properly understand coating properties and to develop new ones, the coating microstructure and formation mechanism must be understood by investigating such major factors and interrelations. Recently, there have been many researches concerning the process modification and most of them have focused on the control of the energy combination of the in-flight particles.[2,3] And this energy combination of the in-flight particles depends on gas flow rate, spray distance, powder feed rate and particle size.

In applications for bioceramic coatings, the adhesion strength of the coating to the implant surface and the surface roughness and the porosity of implant surface appear to be a properties that needs to be optimized to avoid cracking, shearing off and chipping of the bioactive coating such as Hydroxyapatite(HA) during emplacement of the implant[4,5] and osseointegration between the bone and the implant.[6,7]

To achieve improved adhesion between substrate and HA coating layer and to increase the biological responses of bone to the implant surface, this paper deals with the development of biocompatible TiO_2 coating by the Taguchi analytical method and evaluate their potential uses as a bioceramic coating layer for load bearing implants. In addition, the contents of this work will be used for the detailed investigation of the bioactive layer/bond layer/substrate coating system.

2. Experimental Procedures

2.1. Specimen preparation and coating

Ti-6Al-4V ELI (ASTM F136-92) plates (70 mm×50 mm ×2 mm) were used as a substrate. The feedstock material was 99% TiO_2 powder in purity (Metco 102 powder) and the TiO_2 particle was prepared by fusing and crushing methods. The particle shape was angular/blocky and particle size range was −88+7.8 μm. The substrate was ultrasonically cleaned with acetone and alcohol, Al_2O_3 grit-blasted and then placed into an Air Plasma Spray(APS) system (Metco 9M system) for TiO_2 coating. The arc current was fixed at the value of 500A.

2.2. Taguchi matrix setup

In this study, we used the basics of the Taguchi technique to determine and partially quantify which deposition vari-

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ables had the greatest influence on the properties of APS TiO_2 coating. The Taguchi technique is a statistical method which is used to efficiently determine the influence of various variables on a given process;[8-10] in this case, the plasma spraying of TiO_2 ceramics. Increased efficiency is achieved by the use of orthogonal arrays which allows engineers to study a small fraction of the possible combination of factors. The Taguchi technique has the ability to select different sized matrices to suit the number of variables to be examined. Four variables with three levels which are considered to be an important factor in APS coating system were chosen, therefore an $L_9(3^4)$ matrix was determined to be the most suitable. An $L_9(3^4)$ matrix can study four variables and three levels with only nine experimental runs.

Table 1. Taguchi Matrix Variables and Constants

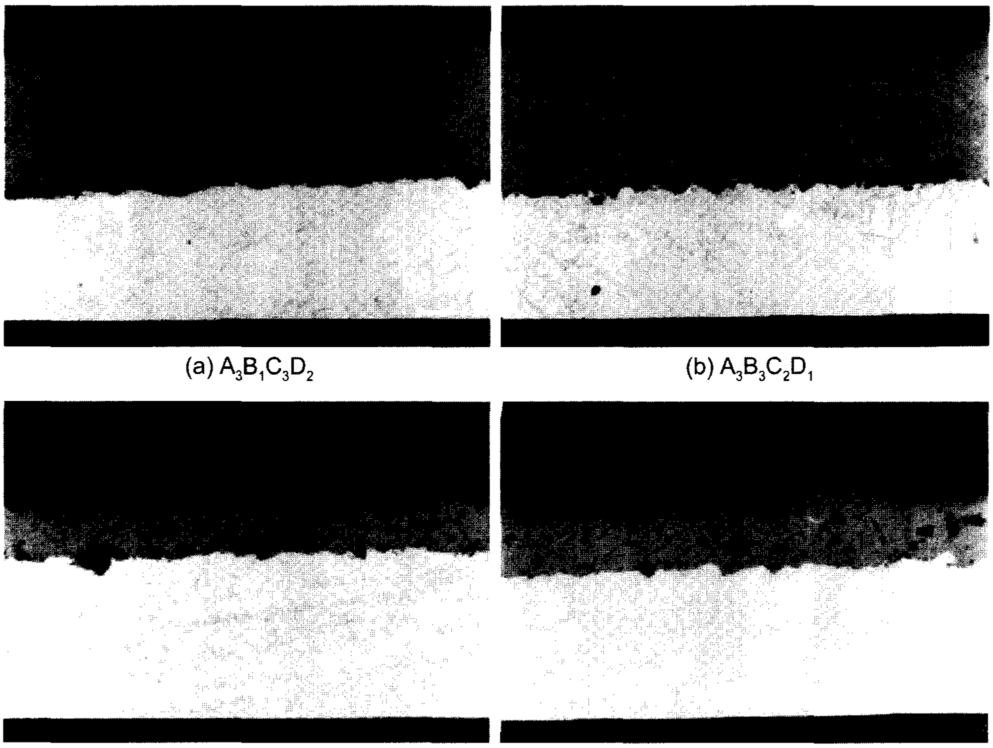
No. of Experiment	H_2 gas flow rate (A)	Spray Distance (B)	Powder Feed Rate (C)	Ar gas flow rate (D)
1	5(1)	65(1)	20(1)	75(1)
2	5(1)	80(2)	30(2)	100(2)
3	5(1)	95(3)	40(3)	125(3)
4	10(2)	65(1)	30(2)	125(3)
5	10(2)	80(2)	40(3)	75(1)
6	10(2)	95(3)	20(1)	100(2)
7	15(3)	65(1)	40(3)	100(2)
8	15(3)	80(2)	20(1)	125(3)
9	15(3)	95(3)	30(2)	75(1)

Constants	Variables	Levels		
		1	2	3
Gun : Metco 3MB	Primary gas (Ar) flow rate (SCFH)	75	100	125
Nozzle : Metco 531	Secondary gas (H_2) flow rate (SCFH)	5	10	15
Primary gas pressure : 100 psi	Spray distance (mm)	65	80	95
Secondary gas pressure : 50 psi	Powder feed rate (g/min)	20	30	40

Table 1 outlines the Taguchi matrix where the columns represent the plasma spray variables with appropriate three levels chosen for each variable and the rows represent the nine experimental spray runs. Analysis of the interaction affects has been excluded from this study.

2.3. Tests of coating properties

All specimens were sectioned with a diamond saw and then the specimen was epoxy mounted and fine-polished to minimize the smearing and pull-out of particles. Optical microscopy (Leica Leitz DMR, Germany) and SEM (JEOL 6400, Japan) were used to characterize the microstructure of the coating layer and coating/substrate interface. Porosity and pore size were measured with an image analyzer (Image pro v4.0, Switzerland). The roughness of grit-blasted substrate as well as the various plasma sprayed surfaces was measured using a surface roughness tester (Mahr sur-



(a) $A_3B_1C_3D_2$ (b) $A_3B_3C_2D_1$

(c) $A_1B_3C_3D_3$ (d) $A_1B_2C_2D_2$

Fig. 1. Cross-sectional morphology of as-sprayed TiO_2 coatings.

fanalyzer 5000, Germany). The measured length was 10 mm at a probe speed of 0.25 mm/s. Vicker's microhardness (Shimadzu HMV-2000, Japan) was measured on the normal to the coating surface that had been polished down to the 3 μm DP-spray. Indentation conditions were set to a 300 g-force for 15 s.

3. Results and Discussion

In this experiment, analytical results of the coating properties could be divided into two groups. The one thing is Smaller-the-Better(SB) and the other is Lager-the-Better(LB). The coating thickness and pore fraction could be served as a SB case. If TiO_2 powders are well melted in a plasma jet stream and have efficient impact velocity, the lamellar structured splat would be formed through flattening and rapid solidification processes as shown in Fig. 1(a) and (b), thus the coating thickness would be decreased. Then, the residual stresses which reduce the life-time of coating also would be decreased. Moreover, if the denser coating would be obtained by reduced pore size and uniform pore distribution, the more durable coating could be achieved and hinder the occurrence of the detached fragments that have very adverse effects on the implant or tissues surrounding it. As shown in Fig. 1(c) and (d), large sized pores which is formed by the unmelted particles and the irregular splashing of impacting particles, are existed in the coating layer. Such defects in the coating layer may promote unwanted invasion of acellular connective tissue which may, in turn, lead to aseptic loosening of the implant as a result of micromotions during the initial phase of the healing process.[13] On the other hand, the surface roughness and microhardness could be served as a LB case. The surface roughness has been increased, giving the implant surface texture with an enlarged surface area. Upon insertion the implant, the early bone healing phase is enhanced by the increased titanium oxide surface and this surface is known to accelerate the initial healing phase through absorption of protein, the accumulation and activation of platelets, fibrin retention and consequently an increased amount of surrounding bone.[14] Besides, the microhardness is correlated with strength that is one of the representative properties, as the microhardness value increased, the beneficial effect of plasma spray coatings also increased.

Above mentioned properties of TiO_2 plasma spray coating are explained as follows.

3.1. Effects of the process parameters on the coating properties

The mean values of the thickness, surface roughness, microhardness and porosity of the coating from Taguchi parameters are shown in Table 2 and ANOVA(Analysis of Variance) on the mean values of the properties would be performed in order to evaluate the effects of the process parameters more quantitatively and ANOVA results for them are shown schematically in Fig. 2.

Table 2. Coating Properties from Taguchi Parameters

No.	Coating thickness (μm)	Surface roughness (Ra)	Microhardness ($Hv_{0.3}$)	Porosity (%)
	Mean value	Mean value	Mean value	Mean value
1	65	6.24	766	3.411
2	60	5	593	4.991
3	50	4.23	615	5.061
4	40	6.46	744	4.262
5	55	6.16	824	5.154
6	90	4.90	676	5.146
7	150	8.08	828	2.085
8	50	5.82	755	5.123
9	150	5.26	849	1.34

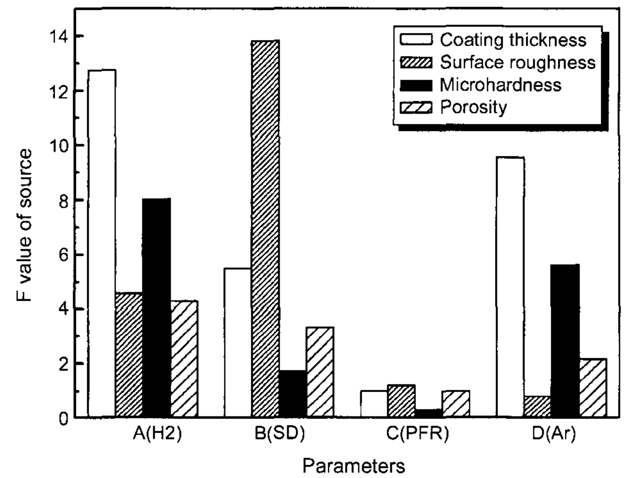


Fig. 2. F value of process parameters on the coating properties.

F value of powder feed rate is smallest, so effect of the powder feed rate on the coating thickness is negligible. The plasma gas compositions or the H_2 gas flow rate and Ar gas flow rate were the most important factors that affected the coating thickness. The coating thickness increased as the hydrogen fraction in the plasma jet increased. The spraying power generally increased with the increase of the total gas flow rate. The effect of the hydrogen was more marked than that of the argon. In fact, coating could not be obtained when it was sprayed using pure Ar plasma gas. That is to say, the coating thickness may be strongly dependent on the thermal energy of an impacting particle or H_2 gas flow rate.

Spray distance and H_2 gas flow rate were the important parameters that affected the surface roughness and especially the effect of the spray distance was more conspicuous than that of the other spray parameters. As the spray distance decreased, the surface roughness value(R_a) increased. This may be due to the increase on the degree of the unmelted particles, irregular impacting particles and accumulation layers by transferring insufficient thermal energy within very short time interval. The surface roughness of the grit blasted substrate is somewhat uniform, so the vari-

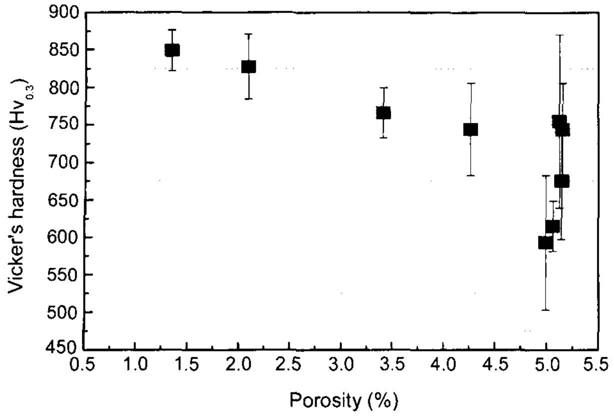


Fig. 3. Vicker's microhardness according to the porosity.

ance of surface roughness only by process parameters is reliable. From the biological point of view between bone and biomaterial interface, the enlarged surface area by increasing surface roughness would have given the beneficial effect on the implant materials.

The H_2 gas flow rate and Ar gas flow rate were the most important factors that affected the microhardness. The increase of hydrogen gas fraction in a plasma jet raises the enthalpy and the thermal diffusivity of the plasma jet and thus the melting state of an in-flight particle is expected to increase. On the other hand, the increase of the total gas flow rate decreases the residence time of the particle in the plasma jet. This implies the shortness of the heat interaction time between particle and plasma jet. Virtually, as shown in Fig. 3, the microhardness of the coatings shows the dependence on the coating porosity that also was dependent on the melting state. Therefore, in terms of the heat transfer reaction between an in-flight particle and a plasma jet, the melting state of TiO_2 powder is expected to increase from a partially melted state to a fully melted state when it is injected into a plasma jet having higher H_2 gas flow rate and lower Ar gas flow rate.

The H_2 gas flow rate, Ar gas flow rate and spray distance were major factors that affected the porosity fraction. But, the difference of contribution degree of process parameters were relatively smaller than that of the others. This means that the mechanism of formation of pore is relatively complicated and the pore morphology must be also considered but, within the scope of this study, only numerical value of porosity fraction is presented. However, the porosity has a closer correlation with the H_2(thermal energy term) and spray distance(thermal energy transfer term) than the Ar(kinetic energy term), which has been confirmed by other researchers.[11,12] Also when the pore morphology is considered, it has been found that small sized pores mainly resulted from the entrapped gas during plasma spraying while large sized pores might result from the presence of unmelted particles or the splashing of impacting particles. Therefore, process parameters such as plasma gas composition and spray distance must be considered mainly to reduce the porosity within the coating layer.

Table 3. Recommendation Parameter Levels and Estimated Results in Terms of Surface Roughness and Porosity

A	B	C	D	Surface roughness, R_a	Porosity (%)
3	1	3	2	8.08	2.09
3	1	2	2	7.5	1.52
3	1	3	1	7.97	1.31
3	1	2	1	7.39	0.74

3.2. Determination the optimized plasma spray coating parameter

The above mentioned results have shown that the H_2 gas flow rate and Ar gas flow rate were the most important factors that affected the coating thickness and microhardness. Moreover, the spray distance was the most important factors that affected the surface roughness of the coating and the H_2 gas flow rate, Ar gas flow rate and spray distance were major factors that affected the porosity fraction though the difference of contribution degree of process parameters were relatively smaller than that of the others. First of all, to increase the surface roughness and decrease the porosity fraction in the coating layer were considered to optimize the plasma spray coating condition because the surface contact area between bone and implant surface and coating durability closely relation to porosity fraction, size and location would can be the most important factors in the biological environment. In view of the high thermal energy of H_2 and transferring insufficient thermal energy within very short time interval due to short spray distance, recommendation parameter levels and estimated results in terms of surface roughness and porosity were presented in Table 3. As shown in Table 3, the surface roughness value was not so decreased sharply and porosity fraction showed remarkable decrease relatively when the powder feed rate was 30 g/min and the Ar gas flow rate was 75 SCFH. Therefore, the recommendation parameters for the application of biomaterials as an implant, is an $A_3B_1C_3D_1$ and the expectation value of surface roughness value (R_a) and porosity fraction were 7.97 and 1.31%, respectively.

4. Conclusions

In this study, the effects of the plasma spray coating process parameters on the coating thickness, surface roughness, microhardness, porosity were investigated using a fused and crushed TiO_2 powder by Taguchi method. The coating thickness and porosity fraction could be served as a SB case and the surface roughness and microhardness could be served as a LB case. The H_2 gas flow rate and Ar gas flow rate were the most important factors that affected the coating thickness and microhardness. As the spray distance decreased, the surface roughness value(R_a) increased due to the increase on the degree of the unmelted particles, irregular impacting particles and accumulation layers by transferring insufficient thermal energy within very short time interval. In case of porosity, the H_2 gas flow rate, Ar gas flow rate and spray distance were major factors that affected the porosity. But, the difference of the contribution degree of process parameters were relatively smaller than that of the others.

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