

Journal of Korean Institute of Surface Engineering  
Vol. 29, No. 6, Dec., 1996

## THE EFFECT OF SPRAYING PARAMETERS ON THE PROPERTIES OF HYDROXYAPATITE COATING

K. S. Park\*, W. T. Huh\*, Y. H. Son\*, C. K. Kim\*, S. Y. Kim\*\*,  
S. G. Kim\*\*\* and S. W. Kim\*\*\*

\* *New-Tech Co., Ltd, Dalseogu Wolamdong Seongseo Industrial Area Zone 2-2, 37B 7L, Taegu*

\*\* *Department of Materials Engineering, Yeungnam University, Kyongsan, Taegu*

\*\*\* *Production Technology Center, KAITECH, Seogu, Kajwadong 472, Incheon*

### ABSTRACT

Plasma spraying process was employed to produce HA coating on Ti6Al4V alloy for the development of a dental implant. The goal of this research was to find optimum spraying conditions for HA coating on Ti6Al4V. This study was thus designed carefully to evaluate how spraying parameters affect various physical properties of a HA coating layer, such as phase composition and bond strength. In plasma spraying, spraying parameters such as hydrogen flow rates and spraying distances were varied systematically to change the degree of the melting of starting HA powder in plasma jet. It was revealed that the deposition efficiency increased with increasing a hydrogen flow rate, and the bond strength between the HA-coated layer and Ti-alloy substrate increased with hydrogen flow rate, but decreased with spraying distance. Therefore, the hydrogen flow rate and the spraying distance should be carefully controlled to obtain the reasonable bond strength simultaneously.

### INTRODUCTION

Hydroxyapatite or simply HA,  $\text{Ca}_{10}(\text{P}_2\text{O}_7)_6(\text{OH})_2$ , has been a very promising bioceramic material which can be used for prostheses to replace damaged parts of a human body. The main reason for the commercial success of this material lies in the firm and fast fixation to the bone<sup>(1)</sup>. Since bulk HA possess a low tensile strength, HA has been widely used as a coating material on metal implants by plasma spraying<sup>(2-3)</sup>. The performance HA coated implant largely depends upon the characteristics of the HA coating such as

coating thickness, surface roughness, porosity, bond strength, and phase compositions<sup>(4-9)</sup>. All these characteristics are affected by plasma gas composition, plasma spraying conditions, and starting HA powder, and so on.

However, it is very difficult to find the best spraying procedure to get a high quality of the HA coating. It was noted in many literatures<sup>(4-6)</sup> that controlling the degree of melting of starting HA powder is of primary importance to cope with this problem. When Ar-H<sub>2</sub> gas mixture is used in plasma spraying, the problem can be accomplished by controlling the hydrogen flow rate and the spraying

distance. Therefore, this study was designed how these two parameters affect the coating quality. The goal of this study is to find optimum spraying parameters for commercially available HA powder.

## EXPERIMENTAL PROCEDURES

Ti6Al4V alloy rod having 16mm in diameter was sliced into discs having 6mm thickness. For plasma spraying coating on Ti-alloy discs commercial HA powder was used. The average particle size was 120 $\mu$ m and particle size distribution was between 47 and 180 $\mu$ m in diameter. The several Ti-alloy discs were attached to a steel plate and sand-blasted with 46 mesh alumina grit. The plasma spraying of HA powder was carried out by simultaneous rotating the steel plate and traversing the spraying gun across the discs.

The plasma spraying system used, so called Hexaplasma which has a maximum 80kW power. The feed rate was 15g/min, the primary gas, Ar, flow rate 70L/min, the current 600A, and the powder carrier gas Ar. As shown in Table 1, the hydrogen flow rate and the spraying distance were controlled to change the degree of melting of HA powder in the plasma jet.

In order to measure the HA film thickness, HA-coated alloy discs were separated from the steel plate, then an alloy disc was sectioned by a diamond impregnated saw, and mounted in the bakelite. The film thickness was measured under a light microscope after polishing a mounted sample. The deposition efficiency of HA film was calculated by using the equation 1. The bond strength between HA-coating layer and Ti alloy disc was mea-

sured two to six times using a tensile testing machine (Sebastian V). The test was done by attaching 6mm Al stud to the surface of the coating, curing for 1 hour at 150°C, and then pulling down the Al stud against the coating surface.

The morphology of HA-coating surface was examined by a scanning electron microscope (Hitachi Co.). The phase composition of HA-coating layer was investigated by X-ray diffractometer (Rigaku) with Cu-K $\alpha$  target and the scanning rate was 2°/min. In order to examine the dehydroxylation of HA powder during plasma spraying, FTIR analysis was done.

Table 1. Spraying parameters for HA coating

Specimen Number	Hydrogen Flow Rate (L/min)	Spraying Distance(mm)
A	1	85
B	1	100
C	1	115
D	1	130
E	3	85
F	3	100
G	3	115
H	3	130
I	5	100
J	12	100

## RESULTS AND DISCUSSION

### Deposition Efficiency

When particles having a certain size distribution are fed into a plasma jet, each particle takes its own trajectory. Therefore, each particle may acquire the different degree of melting and the different velocity at impact. Only a small portion of particles fed into the jet will be accumulated on the surface of a substrate. The deposition efficiency can be defined as the ratio of coating weight and the total

weight of sprayed particles. However, the different method was used to evaluate the deposition efficiency under a given spraying condition in this study. Neglecting the presence of pores in each coating, the deposition efficiency (D.E.) can be estimated as follows.

$$D.E.(%) \frac{VA_d}{rDF} \times 100 \dots\dots\dots (1)$$

where V is the traverse velocity of a gun, A is the area enclosing by two dotted circles in Fig. 1, d is the theoretical density of HA (3.155 g/cc), r is the radius of alloy disc, D is the distance from the center of rotation, and F is the feed rate.

The deposition efficiency for each spraying condition is illustrated in Fig. 2. It increased with the hydrogen flow rate from 6.4% at 1L/min to 23.5% at 12L/min. At relatively low flow rates, the deposition efficiency increased rapidly until 5 L/min. After then, it increased gradually with the hydrogen flow rate. However, the curve of the deposition efficiency should change more steeply with the

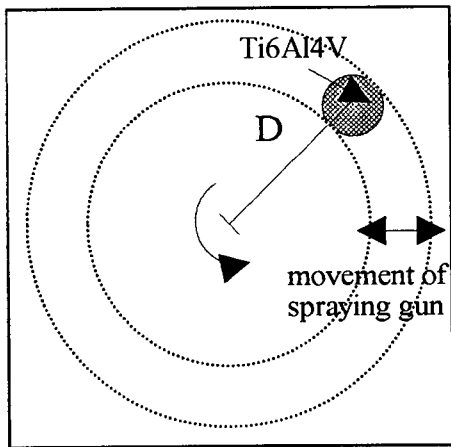


Fig.1 A schematic diagram describing relative movement of alloy discs and gun

hydrogen flow rate since HA coating is dense at a high hydrogen flow rate. In Fig. 2, the deposition efficiency was also evaluated as a function of spraying distance while fixing the hydrogen flow rate to 1L/min. The deposition efficiency dropped slightly at 130mm, but remained constant in the others.

The reason that the deposition efficiency is related to the heat content of the plasma jet, which increases with the hydrogen flow rate. Therefore, the degree of melting of HA powder will increase with the hydrogen flow rate. The results showed that the number of molten particles attached to the substrate increases rapidly up to 5L/min. In the entire range of the hydrogen flow rate, the deposition efficiency was very low since particle size was relatively large.

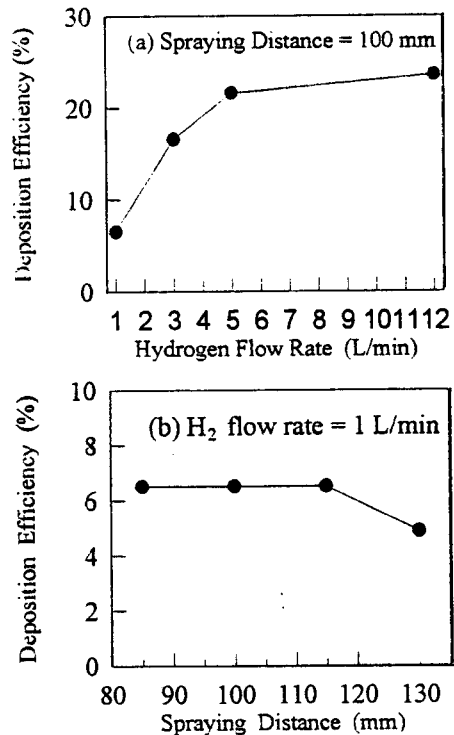


Fig. 2 Deposition efficiency as a function of hydrogen flow rate and spraying distance

The deposition efficiency may also depend upon the spraying distance which it changes the thermal and kinetic history of a particle. As the spraying distance increases, molten particles may resolidify before hitting the substrate and also the number of particles decrease due to the divergent nature from the center of Cu nozzle. Therefore, this may result in the reduction of the deposition efficiency as the spraying distance increases.

### Surface Morphology

The change of surface morphology of a HA-coating layer with different hydrogen flow

rates was illustrated in Fig. 3. Results from various spraying distances were not presented since there was no significant difference in microstructures in this study.

As shown in Fig. 3(a), the microstructure of HA-coated layer exhibits a large amount of unmelted particles, cracks, pores and pancake-like splats. Although SEM micrographs obtained from hydrogen flow rates (3 and 5 L/min) were not given here, their microstructures were similar to that of at 1 L/min. The difference was only that splats were more severely deformed and the number of unmelted particles decreased with the hydrogen flow rate. These severely deformed splats had

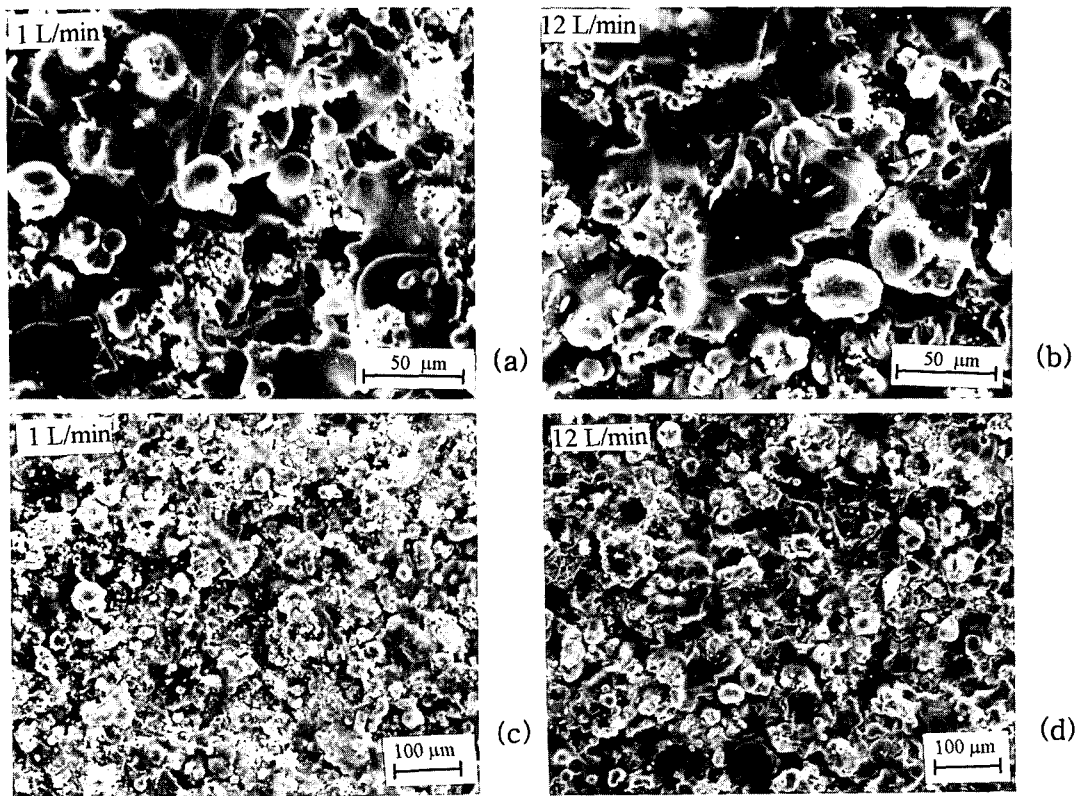


Fig. 3 Surface morphology of HA coating produced by different hydrogen flow rates  
(a) and (c) : 1L/min, (b) and (d) 12L/min

more irregular edges than the others. On the other hand, the microstructure corresponding to 12L/min contained little amount of unmelted particles so that the surface of HA-coated layer was covered by the solidified powder. The microstructural difference between two hydrogen flow rates (1 and 12L/min) can be seen clearly by comparing Fig. 3 (c) and (d).

Cracks on the HA-coated layer is usually found in plasma sprayed coating as a result of stress relief. And the unmelted particles can be originated from two sources; one is purely unmelted in the plasma jet and the other one is owing to naked particles by pulling off the melted part of partially melted particles at impact. The pores is due to the insufficient deformation of molten particles at impact<sup>(6)</sup>.

### Phase Composition

X-ray diffraction patterns were obtained for HA coating on Ti6Al4V discs as well as the starting HA powder. Fig. 4 illustrated the XRD patterns for HA-coated layer obtained by varying the hydrogen flow rate at a constant spraying distance (100mm). Peaks were analyzed with JCPDS cards of HA,  $\text{Ca}_4\text{P}_2\text{O}_9$  (TP),  $\alpha$  and  $\beta$ - $(\text{Ca}_3\text{PO}_4)_2$  (TCP), and CaO compounds. The main peaks of these compounds occur when  $2\theta$  is equal to 31.8, 29.7, 30.7, 31.0 and 37.2°, respectively.

In Fig. 4, the starting HA powder was highly crystalline, but included small amount of impurity phases. When the hydrogen flow rate was 1L/min, the background shift in the XRD pattern was observed, which indicates the presence of amorphous phase due to the

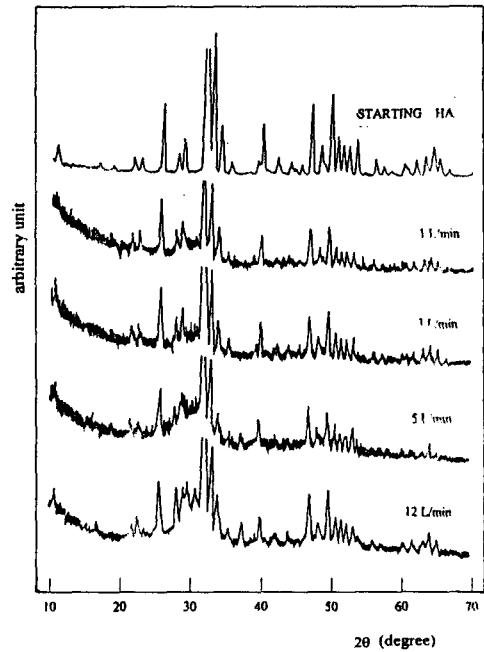


Fig. 4 X-ray diffraction patterns of starting HA and diffraction HA coatings

rapid cooling of molten particles. Also small amount of TP and TCP phases were detected. However, CaO compound was not found. However, as the hydrogen flow rate increased over 5 L/min, amount of impurity phases such as TP and TCP as well as amorphous phase increased significantly. And it was noted that a peak for CaO compound was detectable. Moreover, the peak intensity of CaO compound became strong as the hydrogen flow rate increased.

The FTIR spectra of starting HA powder and coated HA powder were illustrated in Fig. 5. O-H absorption bands at 627 and 3572  $\text{cm}^{-1}$  were disappeared in the plasma sprayed HA. Therefore, it is noted that starting HA is dehydroxylated during plasma spraying.

In general, the plasma spraying of HA is

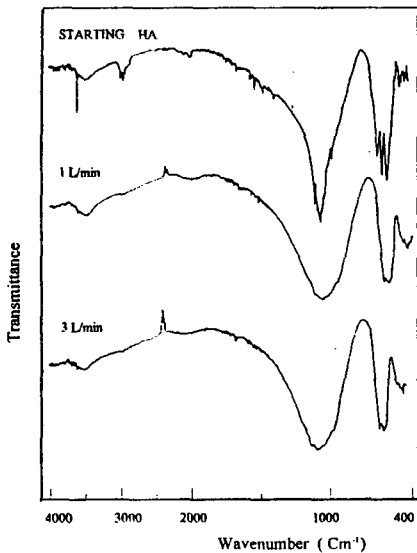


Fig. 5 FTIR spectra of starting HA and different HA coatings

conducted at very low deposition efficiency, and it is very difficult to avoid the phase decomposition of HA due to a high temperature during plasma spraying process. The amount of these impurity phases, especially the amorphous phase, should be minimized since it is much more resorbable in a living body than crystalline HA. It was shown that the amount of impurity phases introduced by a decomposition of HA was proportional to the heat amount in which HA powder received during their flight in the jet. Therefore, it is necessary to control the degree of the melting of HA powder so that only the surface of HA powder may be melt. As shown in Fig. 3, this was achieved to some extent by minimizing the hydrogen flow rate.

Beside a resorption problem of impurity phases, there is an another issue such as biocompatibility in a living body. It should be noted that CaO compound is the most detrimental phase since it is not biocompatible at

all<sup>(5)</sup>. Therefore, the formation of CaO during plasma spraying should be restricted. In this study, it was avoided by using a low hydrogen flow rate less than 3L/min. However, the amount of other impurity phases can be eliminated or minimized by a post heat-treatment<sup>(10)</sup>.

### Bond Strength

The bond strength between the HA coating and Ti-alloy substrate is very important factor in determining the performance of an implant. Some results showed<sup>(8-11)</sup> that failures may occur at the interface between HA coating and Ti substrate rather than between the bone and HA coating.

Fig. 6 showed how the spraying distance affected the bond strength between the coating and the substrate at different hydrogen flow rate. Error bars in Fig. 5 denotes the minimum and maximum values of measured bond strength and black dots denotes the average value. In Fig. 5, the bond strength decreased slightly with the spraying distance. However, the bond strength increased slowly with hydrogen flow rate from 22 kg/cm<sup>2</sup> for 1L/min to 45kg/cm<sup>2</sup> for 12L/min.

In plasma spraying process, the bonding between the HA coating and the Ti-alloy substrate is achieved by flattening molten droplets at impacts and interlocking them mechanically to the asperities on the Ti-alloy surface. It is also possible the diffusion reaction between the HA coating and Ti-alloy substrate during plasma spraying<sup>(12)</sup>. A large hydrogen flow rate will result in a large amount of heat in the jet so that there will be more severe deformation of molten droplets as well as more diffusion in which both of

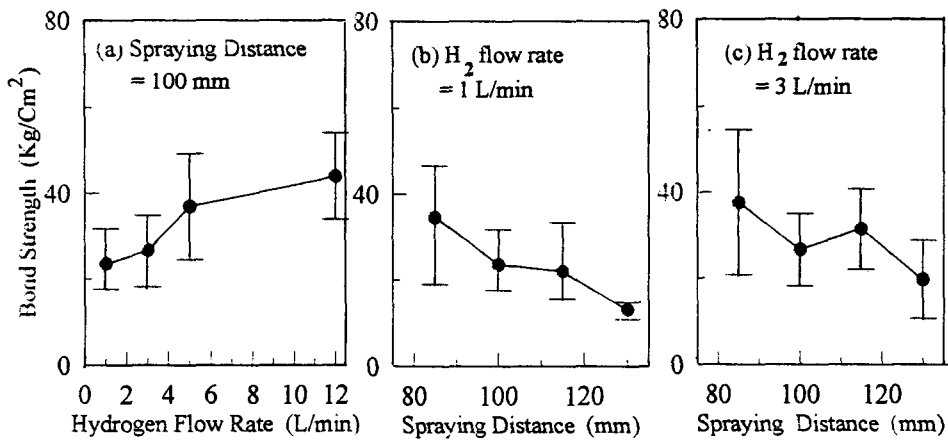


Fig. 6 Variation of bond strength with hydrogen flow rate and spraying distance

fects lead to enhanced the bond strength.

It was mentioned in the previous section that the phase decomposition of HA became severe with increasing hydrogen flow rate. Therefore, the hydrogen flow rate must be optimized to result in reasonable phase decomposition as well as bond strength simultaneously. In this regard, the HA coatings sprayed under conditions B and F in Table 1 is under an animal test in which clinical result will be reported later on.

## CONCLUSION

1) The deposition efficiency was changed steeply in the relatively low range of hydrogen flow rate, i.e. between 1L/min and 5L/min. It can be a useful tool to estimate the degree of melting and the other physical properties as well as the effectiveness of different powder size distribution.

2) The bond strength between the HA-coated layer and Ti-alloy substrate increased with hydrogen flow rate, but decreased with spraying distance. However, the results of the bond strength showed is still low to guaran-

tee a reliable performance.

3) It was is very difficult to avoid a phase decomposition of starting hydroxyapatite powder during plasma spraying. But at least CaO formation was avoided by lowering the hydrogen flow rate.

## ACKNOWLEDGEMENTS

Authors appreciate deeply Professor Seo in Kyungbook National University for XRD and Dr. Shin in Sangsin Co. for SEM. This work was supported by the Ministry of Commerce and Resource, and the Ministry of Health and Welfare.

## REFERENCES

1. L. L. Hench, *J. Am. Ceram. Soc.* **74**, 1487 (1991)
2. K. de Groot et al., *J. of Biomed. Mater. Res.* **21**, 1375 (1987)
3. R. G. T. Geesink et al., *Clin. Orthop.* **225**, 147 (1987)
4. K. A. Khur and P. Cheang, *Proc. of the 1993 National Thermal Spray Conf.*,

- Anheim, CA, USA, 347 (1993)
5. C. Y. Yang et al., *J. of Mater. Sci. : Materials in Medicine* **6**, 249 (1995)
  6. K. A. Gross and C. C. Berndt, 2nd Plasma Techik Symposium, Lucene, Switzland, **3**, 159 (1991)
  7. R. Y. Whitehead et al., *J. of Biomed. mater. Res.* **27**, 1501 (1993)
  8. M. J. Filliaggi et al., *J. of Biomed. Mater. Res.* **25**, 1211 (1991)
  9. B. C. Wang, *Surface and Coatings Technology* **58**, 107 (1993)
  10. J. Weng, *J. of Biomed. Mater. Res.* **30**, 5 (1996)
  11. C. Y. Yang et al., *J. of Mater. Sci. : Materials in Medicine* **6**, 258 (1995)
  12. H. Ji, C. B. Brown, and P. M. Marquis, *J. Of Mater. Sci. : Materials in Medicine* **3**, 283 (1992)