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Fabrication and Characterization of HA/SiO_2 Coatings by Gas Tunnel Plasma Spraying†

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Abstract

Fused silica powder has been mixed with hydroxyapatite (HA) powder and plasma sprayed by using a gas tunnel-type plasma jet. The influence of silica content (10 Wt. % and 20 Wt. %) on the microstructure and mechanical properties of HA-silica coatings was investigated. The spraying was carried out on a SUS 304 substrate in an atmospheric chamber. Scanning electron microscope micrographs of cross-sectioned HA/SiO_2 coatings showed that the sprayed samples of 10 and 20 wt.% silica have dense structure with low porosity as well as higher abrasive wear resistance compared to pure HA coatings. As the amount of silica was increased, the coatings become denser, harder and exhibited higher abrasive wear resistance compared to the pure HA coatings.

KEYWORDS: (Hydroxyapatite/SiO_2), (Plasma Spraying), (Microstructure), (Hardness), (Abrasive Wear)

1. Introduction

Permanent metallic prostheses are usually fabricated from light metal or alloys such as Ti and Ti-alloys which exhibit superior mechanical properties such as tensile strength, toughness and fatigue. The surfaces of metallic implants are usually coated with bioactive material to improve the implant integration by promotion the growth of bony tissue (apatite) on the surface of porous biomaterial. Hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$) is the most and established bioactive material which has been used in biomedical application. HA has poor mechanical properties such as fritting fatigue, toughness, abrasive wear and adhesive strength with the implants for load application. Many studies reported the important of silicon in bioactive materials for the bonding of bone and muscle as well as cross-linking agent in connective tissue[1-6]. There are three functions of silicon. First, there is a metabolic function of silicon that is thought to partake in cellular development and gene expression. Second, there is a chemical function as the nature of bonding to bone of bioglasses relates to the in vivo solubility of these glasses that in turn is a function of its silica content. Also, plasma-sprayed silicon-substituted hydroxyapatite was found to enhance formation of bone-like apatite on immersion in simulated body fluid [7].

Third, there is a mechanical function as silica particles appear to improve the strength of a hydroxyapatite coating by particle-mediated reinforcement, leading to crack arrest or crack deflection. From the above information, fused silica (amorphous SiO_2) is a good candidate to improve the mechanical properties of HA coatings. The presence of silica particles inside HA coatings improve the bonding strength among the HA particles and increase the abrasive wear resistance.

Plasma spraying is a well established tool to deposit HA on metallic implants. Many studies were performed to investigate the microstructure, phase transformation, influence of post treatment on the properties of sprayed HA in vitro and in vivo[8-13]. However, the influence of adding silica particles on the mechanical properties of HA coatings has not been investigated yet.

In previous works[14, 15], pure HA coatings were plasma sprayed at different plasma power and spraying distances. The effects of plasma power and spraying distance on the microstructure and mechanical properties were investigated. The results showed that dense, with low porosity and high hardness, coatings are formed as the plasma power increased and spraying distance decreased. The abrasive wear resistance of HA coatings was studied at different plasma power level and the results indicated that, the higher the plasma power, the higher the abrasion resistance of sprayed HA coatings mainly due to the formation of dense with low porosity coatings[16].

In this paper, an attempt to improve the mechanical properties of HA coating by incorporated pure silica particles has been studied. Developed in Osaka University[17-19], a high-power plasma jet known as gas tunnel type plasma torch (GTPS) was used to spray HA coatings on SUS 304 stainless steel substrate. The effects of addition fused silica particles on the microstructure and mechanical properties of HA coatings were investigated. The spraying was carried out in atmospheric chamber.

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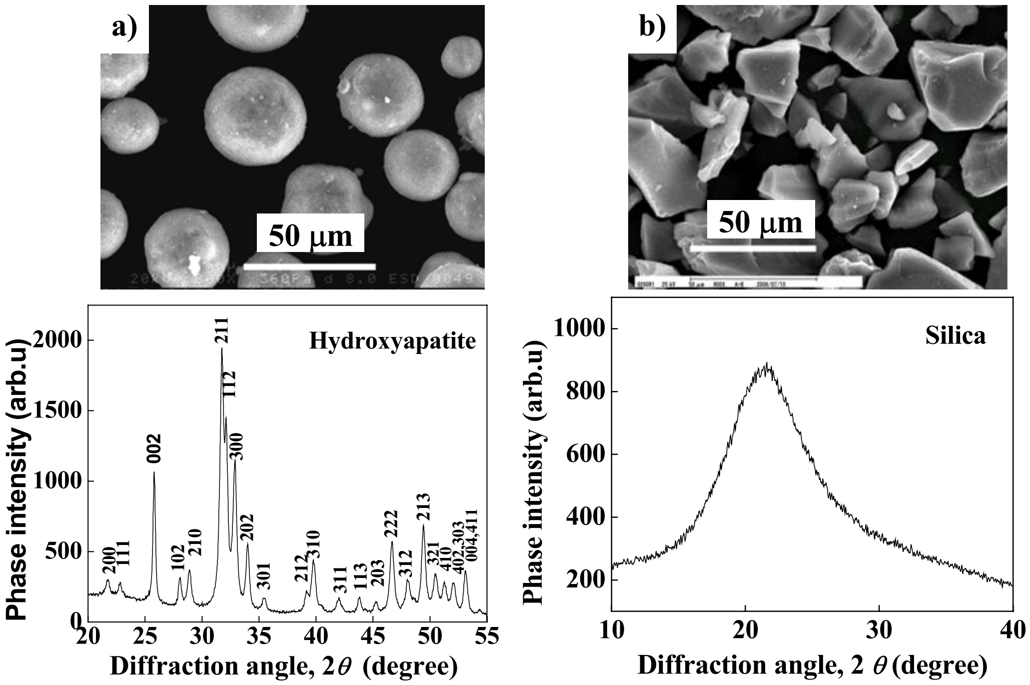

Fig. 1 SEM micrographs and X-ray diffraction patterns of: a) HA powder and b) silica powder.

2. Experimental Procedure

2.1 Materials

Pure HA and silica powders of particle size -10-45 and -10-25 μm were supplied by Pawlex Ltd. Tokyo, Japan and used as spraying materials. The morphology and phase structure of HA and silica powders are shown in **Fig. 1**. The SEM micrographs of the powders indicate that the HA particles are spherical and SiO_2 particles are mainly angular in shape. HA powder is composed of crystalline phase and silica powder is amorphous as shown by X-ray diffraction patterns. HA and silica powders were mechanically mixed and mixtures of HA-10 wt.% SiO_2 and HA-20 wt. % SiO_2 were prepared by stirring the powders together in ceramic pot for 30 min. The mixed powders were plasma sprayed on SUS 304 stainless steel substrate of dimensions 50 x 50 x 2.5 mm. Prior to spraying, the substrate surface was grit blasted with alumina to roughen and clean the surface and followed by cleaning using acetone.

2.2 Gas tunnel plasma spraying

Pure HA powder and mixed HA-silica powders were sprayed by using a gas tunnel type plasma spraying system. A schematic diagram of the gas tunnel type plasma spraying torch is shown in **Fig. 2**. The torch is composed of two copper anodes of diameter 8 mm (internal) and 20 mm (external) and one tungsten cathode. The external anode (vortex) is composed of a circular copper tube and the working gas (Ar) moves inside it in a rotational flow with high velocity. The design of external anode (vortex) allows the plasma gases to move in a tunnel shape which affects the plasma jet shape and increases the efficiency of the spraying process. The gas tunnel generator is composed of a "vortex generator" and a "gas divertor." The vortex generator has many small nozzles arranged in a circle, so that a cylindrically symmetrical vortex flow can be obtained. The whole design and function of gas tunnel plasma torch is found in the reference [18]. The powders were fed externally to avoid over heating and powder decomposition. Before spraying, the substrate was preheated by the plasma jet (600K) to sustain the adhesion of the HA coatings. The spraying parameters are listed in **Table 1**.

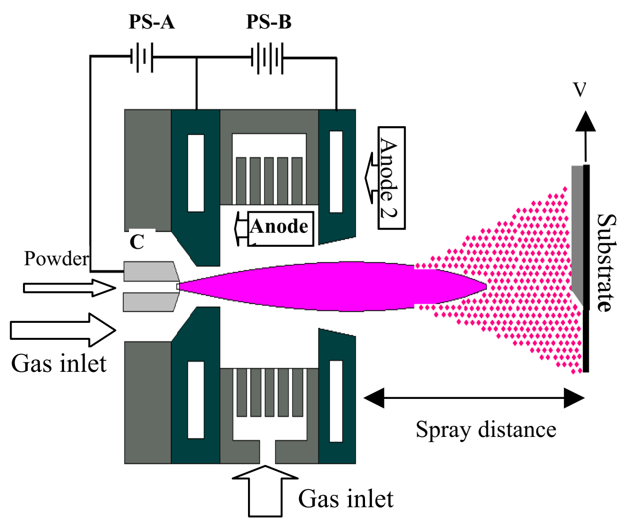

Fig. 2 The gas tunnel type spraying plasma setup.

Table 1 Spraying parameters for HA/ SiO_2 coatings.

Powder	HA/SiO_2
Arc gun current (A)	50
Arc vortex current (A)	450
Gas flow rate (l/min)	150
Carrier gas flow rate (l/min)	7
Powder size (μm)	+10-45
Spraying distance (mm)	60
Substrate traverse speed (mm/s)	40

2.3 Characterization techniques

2.3.1 Microstructure and phase analysis.

Microstructural investigation was carried out on coating surfaces and polished cross-sections. As-sprayed coatings were cut and mounted in hot-resin, followed by grinding and polishing by emery papers and finally mirror finished by buffing using an alumina slurry solution. The morphology of all specimens was investigated using an ERA-8800FE scanning electron microscope. Elemental analysis of coatings was carried out by using electron dispersive spectrometer unit attached with ERA-8800FE SEM. EDX analysis was used to reveal the presence of silica particles inside the coatings.

Phase identification of feedstock and coatings was determined by a JEOL JDX-3530M X-ray diffractometer system with a Cu-K_α radiation source; the operating voltage was 40 kV and the current 40 mA.

Hardness tests were performed on polished and buffed cross-sections of coated samples using an Akashi AAV-500 series hardness tester. The load used was 490.3 mN and the load time was 20 s. Each hardness value is the average of 10 readings.

2.3.2 Abrasive wear test

Abrasive wear tests were carried out using SUGA ABRASION TESTER which follows the NUS-ISO-3 standard. The tested samples were cut from the coated samples with a surface area of 20 x 20 mm^2. The samples were moved horizontally (oscillation mode) a distance of 1cm under load of 25 g on a slightly moved wheel (25 mm/min) covered with SiC emery paper. The width of the wheel is 1 cm and the contacted area with the test sample is 1cm^2. Detailed information about the abrasive wear tester is found in Ref. [16].

The starting thickness of tested HA coatings was 300 μm. The test sample was exposed to move against the abrasive wheel at different loading times (5-190 sec) and the weight loss was measured using a 6 digit electronic balance. The abrasive wear test was performed in dry conditions in an air atmosphere at room temperature.

3. Results and Discussion

3.1 Morphology and phase structure of HA-SiO_2 coatings

Fig. 3 shows the scanning electron micrographs of coatings cross-sections corresponding to pure HA, HA-

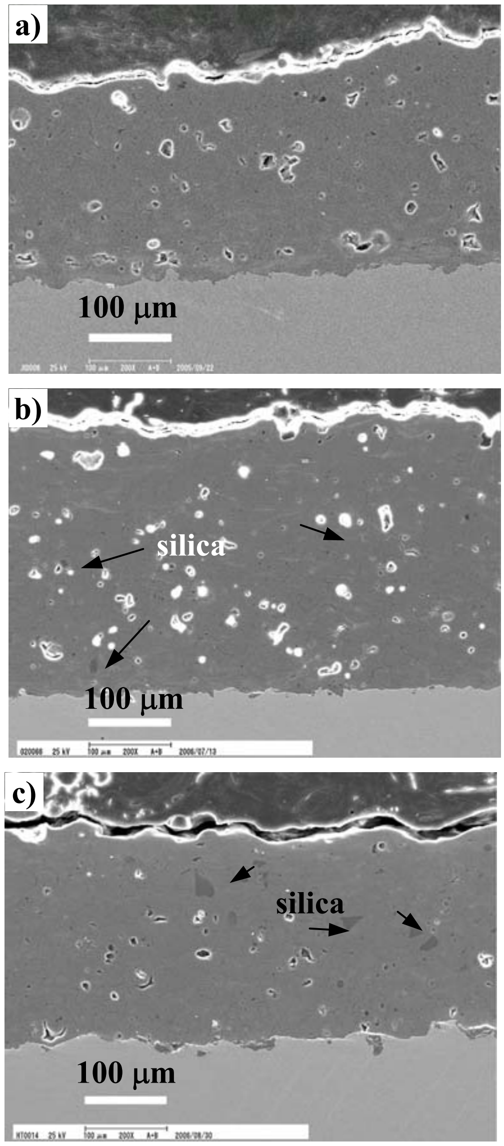

Fig. 3 SEM micrographs of: a) pure HA coatings, b) HA-10 wt.% SiO_2 and c) HA-20 wt.% SiO_2.

10 wt.% - SiO_2 and HA-20 wt.% - SiO_2 coatings. It is clear from the micrographs that the coatings porosity decreases and their structure become denser as the silica contents increase. Additionally, silica particles are visible inside HA coatings matrix and their volume fraction increases with increasing the silica wt. percentage. All the coatings have thickness ranging from 300-400 μm with good adhesive strength with the substrate where there are no visible cracks appearing at the interface or within the coatings. The presence of pores refers to the poor cohesion bonding between adjacent splats as well as the presence of unmelted particles. The coatings porosity is slightly improved by increasing the silica contents (20 wt %) because the high melting points of fused silica (~1800 ^oC) may increases the temperature of HA particles and decreases the number of unmelted HA

particles. It is known that more complete particle melting usually results in a lower porosity contents.

X-ray diffraction patterns of pure HA and HA/SiO_2 coatings are shown in **Fig. 4**. The structure of pure HA and HA/SiO_2 coatings is composed of HA phase and all the peaks match the JCPDS 9-432 card. However, the HA peaks became less sharp and broadened as the silica contents increase because the increase in the volume fraction of the amorphous silica phase. The presence of amorphous silica particles affects the crystallinity of HA-silica coatings mainly due to the increase of the melting degree of HA particles. The same result was obtained by increasing the input plasma power studied by Y.C. Tsui et al. [20]. They found that the coatings crystallinity decreases as the input power increases due to the increase of particle temperature. In our case, the high melting point silica particles adjacent to or contact with HA particles increases their melting temperature degree. Silica phase does not exist in X-ray diffraction patterns because of its amorphous structure.

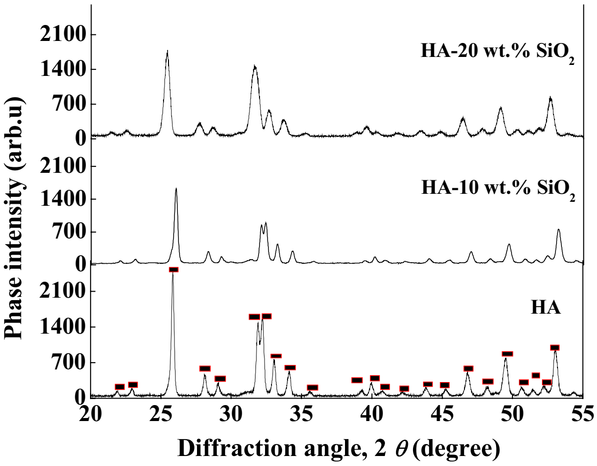

Fig. 4 X-ray diffraction patterns of pure HA coating and HA/SiO_2 coatings.

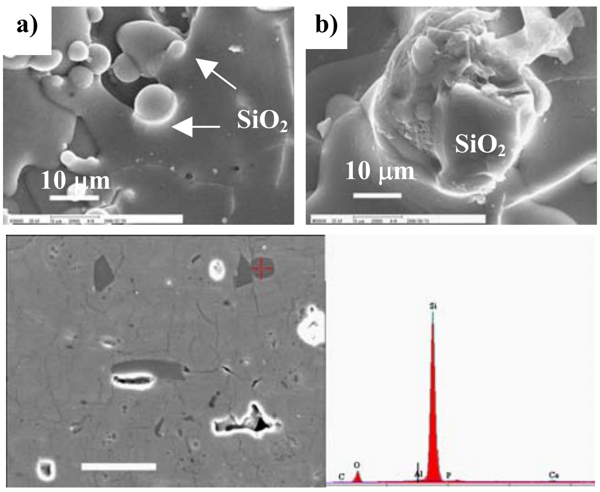

Fig. 5 SEM micrographs and EDX analysis of HA/SiO_2 coatings surfaces: a) HA-10 wt.% SiO_2 and b) HA-20 wt.% SiO_2 and c) point analysis (EDX) of HA-20% SiO_2 showing silica particles.

3.2 Surface morphology and EDX analysis

Scanning electron microscope micrographs of HA-silica coatings surfaces and EDX analysis are shown in **Fig. 5**. There are many spherical particles distributed on the surface and inside the HA coatings. By EDX analysis it was found that many of these particles are melted and unmelted silica particles. Spherical silica particles have been found inside the coatings which indicate that the silica particles were melted and deformed from irregular to spherical shape. However, in the other photo the silica particle is still irregular in shape. From the surface morphology of HA-silica coatings, it is found that small silica particles (< 5 μm) are semi- or fully melted and large silica particles (> 7 μm) are unmelted. However, the majority of HA particles are fully melted and mechanically adhered together in dense manner with silica particles.

EDX point analysis was performed for the HA-20 wt.% silica coating cross-section as shown in **Fig. 5c**. The target of the point analysis was a particle (dark gray) incorporated in the HA matrix. The analysis showed strong peaks of Si and oxygen which indicates the presence of SiO_2 particles.

3.3 Hardness

Hardness of pure HA and HA-silica coatings were measured to investigate the influence of incorporated silica on the mechanical properties of HA coatings. Hardness values of the coatings are shown in **Fig. 6**. The hardness of the sprayed HA-silica coatings was slightly increased compared with the pure HA coatings because of the decrease of coating porosity and increase of the bonding strength of HA by adding silica.

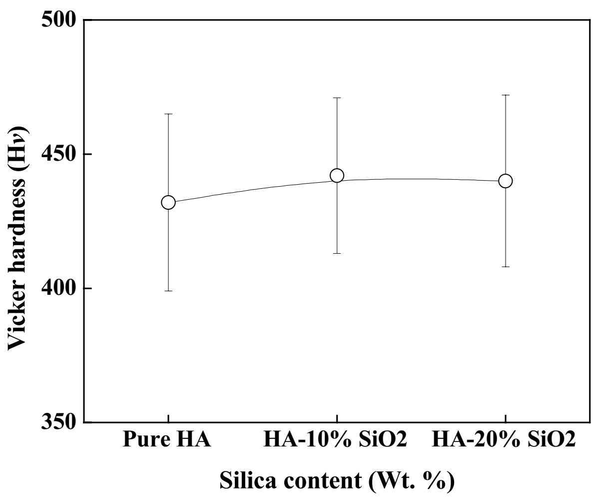

Fig. 6 Hardness of pure HA and HA-silica coatings.

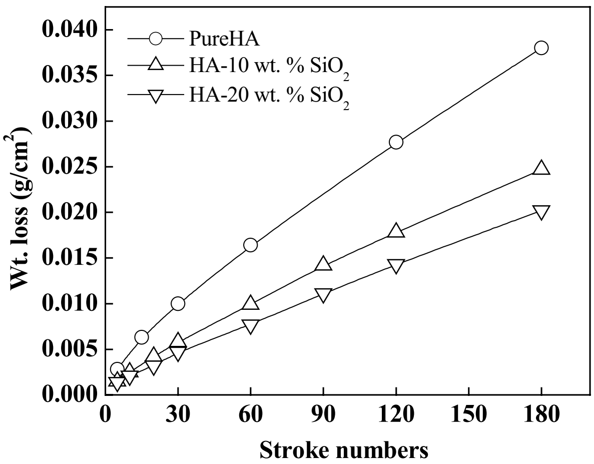

Fig. 7 Abrasive wear resistance of pure HA and HA-silica coatings.

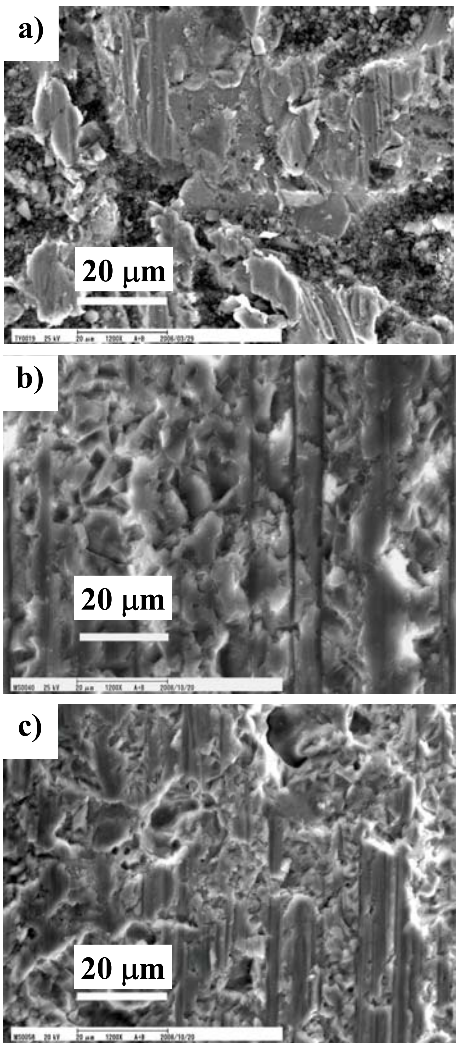

Fig.8 SEM micrographs of surfaces of HA-SiO_2 coatings after abrasion test: a) pure HA b) HA-10% SiO_2 and c) HA-20% SiO_2.

3.4 Abrasive wear

The abrasive wear resistance was tested for pure HA coatings and HA-silica coatings. The abrasive wear behavior of the coatings is shown in **Fig. 7**. It was found that the abrasion resistance was significantly improved for HA coatings reinforced with silica particles as compared with pure HA coating. The abrasive wear rate is 0.016, 0.0099 and 0.0077 g/cm^2/min for pure HA, HA-10% SiO_2 and HA-20% SiO_2 respectively. The data of abrasive wear rate indicated that the abrasion resistance was increased by increasing the silica contents. The presence of silica particles, which acts as a self lubricant, improves the abrasive wear resistance of sprayed HA coatings. The surface morphology of pure and HA/SiO_2 coatings after abrasion test is shown in **Fig. 8**. The morphology of the surface of pure HA coatings exhibits many pores and damaged areas with cracks. However, the surfaces of HA/SiO_2 coatings showed more smooth surfaces with fewer damaged areas. The presence of silica, which is distributed inside the coatings, acts as lubricant for any friction occurring at the coating surface.

4. Conclusions

Pure HA and HA-silica coatings were plasma sprayed by using gas tunnel type plasma torch. The influence of silica contents on the microstructure and mechanical properties of the resulting coatings was investigated. The results can be summarized as follows:

(1) Scanning electron micrographs showed that the porosity slightly decreased and the coatings become denser as the silica contents increased.
(2) Silica particles have been seen inside HA coatings matrix and their volume fraction increased with increasing the silica wt. %.
(3) From the surface morphology of HA-silica coatings, fine silica particles (< 10 μm) were deformed into spherical shape but large particles (> 10 μm) were still irregular in shape.
(4) The hardness of the sprayed HA-silica coatings was slightly increased compared with the pure HA coatings because of the decrease of the coating porosity.
(5) The abrasive wear resistance of HA coatings was significantly improved by adding silica particles because they act as self-lubricant.

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References

1) Carlisle EM. Silicon: a possible factor in bone calcification, Science, 167 (916) (1970) 279–80.

2) Schwarz K, Milne DB. Growth-promoting effects of silicon in rats, Nature 239 (5371) (1972) 333–4.
3) Schwarz K. A bound form of silicon in glycosaminoglycans and polyuronides. Proc Natl Acad Sci USA 70(5) (1973) 1608–12.
4) Hench L, Paschall H. Direct chemical bond of bioactive glass-ceramic materials to bone and muscle. J Biomed Mater Res. 7(3) (1973) 25–42.
5) Gao T, Aro HT, Ylanen H, Vuorio E, Silica-based bioactive glasses modulate expression of bone morphogenetic protein-2 mRNA in Saos-2 osteoblasts in vitro, Biomaterials 22(12) (2001) 1475–83
6) Karin A. Hing, Peter A. Revell, Nigel Smith, Thomas Buckland, Effect of silicon level on rate, quality and progression of bone healingwithin silicate-substituted porous hydroxyapatite scaffolds, Biomaterials 27 (2006) 5014–5026.
7) Hijón et al., Acta Biomater. 2(5) (2006) 567-574.
8) V. Guipont, M. Espanol, F. Borit, N. Llorca-Isern, M. Jeandin, K.A. Khor, P. Cheang, High-pressure plasma spraying of hydroxyapatite powders, Materials Science and Engineering A325 (2002) 9–18.
9) Hong Liang, Bing Shi, Aaron Fairchild, Timothy Cale, Applications of plasma coatings in artificial joints: an overview, Vacuum 73 (2004) 317–326.
10) Yi-Pang Lee, Chih-Kuang Wang, Tsui-Hsien Huang, Chun-Cheng Chen, Chia-Tze Kao, Shinn-Jyh Ding, In vitro characterization of postheat-treated plasma-sprayed hydroxyapatite coatings, Surface & Coatings Technology 197 (2005) 367– 374.
11) Robert B. Heimann, Richard Wirth, Formation and transformation of amorphous calcium phosphates on titanium alloy surfaces during atmospheric plasma spraying and their subsequent in vitro performance, Biomaterials, in Press.
12) Chuanzhong Chen, Diangang Wang, Quanhe Bao, Liang Zhang, Tingquan Lei, Influence of laser remelting on the microstructure and phases constitution of plasma sprayed hydroxyapatite coatings, Applied Surface Science 250 (2005) 98–103.
13) L. Sevgi Ozyegin, Faik N. Oktar, Gultekin Goller, E. Sabri Kayali, Tokay Yazici, Plasma-sprayed bovine hydroxyapatite coatings, Materials Letters 58 (2004) 2605– 2609.
14) M. F. Morks, Akira Kobayashi, Gas tunnel type plasma spraying of hydroxyapatite coatings, in Proc. of The International Thermal Spray Conference, ITSC May 15-18 2006, Seattle, Washington/USA.
15) M. F. Morks, Akira Kobayashi, Microstructure and mechanical properties of hydroxyapatite coatings prepared by gas tunnel type plasma spraying, International Symposium on Smart Processing Technology, ISMPT 14-15 Nov. 2005, Osaka, Japan.
16) M. F. Morks, Akira Kobayashi, Abrasive wear behavior of sprayed hydroxyapitite coatings by gas tunnel type plasma spraying, N.F. Fahim Wear 262 (2007) 204-209.
17) A. Kobayashi, Y. Arata, and Y. Habara, *J. High Tem. Soc*. Vol 13 (3) (1987) pp 116-124.
18) Y. Arata and A. Kobayashi, *J. Appl. Phys*. 59 (9) (1986) pp 3038-3044.
19) A. Kobayashi, *Weld. International*, Vol 4 (4) (1990) pp 276-282.
20) Y.C. Tsui, C. Doyle, T.W. Clyne, Plasma sprayed hydroxyapatite coatings on titanium substrates Part 1: Mechanical properties and residual stress levels, Biomaterials 19 (1998) 2015-2029.