Colloidal characterization and electrophoretic deposition of hydroxyapatite on titanium substrate

J. MA, C. H. LIANG, L. B. KONG, C. WANG
School of Materials Engineering, Nanyang Technological University, Nanyang Avenue, 639798 Singapore

Hydroxyapatite (HA) powders were prepared by a modified chemical co-precipitation method and electrophoretically deposited onto a titanium tubular substrate. The zeta potential, electromobility and the particle size of the HA suspension was characterized at various pH values and the most stable and dispersed suspension condition was identified. Electrophoretic deposition of the HA particles on the titanium substrate was then carried out at this optimum suspension condition. Studies on deposition rate and examination on the microstructure of the sintered deposit were performed. The stoichiometry of the HA before and after sintering were also confirmed. The deposition experimental data obtained in the present work was also compared with theoretical model proposed in the literature. Lastly, the adhesion strength of the coating was also quantified using shear strength tests.

1. Introduction

For a long time the repair of wear, tear and disease on the human bone has involved the use of materials that were not originally intended for such applications [1]. These materials often are detected as foreign bodies by the patient's immune system and sometimes interact with the body in an undesirable manner. In the recent years, there is huge development in biomaterials that are specially designed to repair and reconstruct damaged or diseased parts of the human bone [2]. Among them, hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, or HA, is the most commonly used material due to its widely accepted biocompatibility [3, 4]. However, a component made of solely HA was found to lack of toughness and can fail catastrophically. As a result, HA coated titanium components, which combine the advantages of the mechanical strength of titanium metal and the bioactivity of HA, are developed and reckoned to be one of the most promising group of implant materials in orthopedic and dental fields.

To coat HA onto the titanium substrate, plasma spray method has been the traditional processing technique. Nevertheless, this technique sometimes gives rise to problems such as non-uniformity in coating density [5], alteration of structure [6], and a wide range of bond strength [7]. In addition, plasma spray does not produce completely crystalline HA layers despite it produces a high temperature stable tetracalcium phosphate [8–10]. Lastly, the process requires the usage of extreme high temperature, which can be as high as 12 000 °C. As a result, researchers have been looking into the development of other coating methods. These methods include ion beam sputtering [11], ion beam dynamic mixing [12], dipping [13], electrophoretic deposition [14], and electrochemical deposition [15]. Among these techniques, there is a growing interest in electrophoretic deposition (EPD) due to its capability of forming uniform coating and simple setup. In addition, it can be used to deposit coating on substrates of complex surface morphology with a wide range of thickness. EPD is also a cheaper technique to produce films of a wide range of thickness compared to the conventional methods such as chemical vapor deposition, sol–gel deposition and sputtering. Sarkar and Nicholson [16] have described that EPD is the deposition of particles in a suspension onto an electrode under the action of an electric field. One of the most important parameters during deposition is the electric field, which is applied through either constant current density or constant voltage across the electrodes in the suspension. A number of reports have been published in the literature [17–23] on direct electrophoretic deposition of oxide materials. Among them, Yamashita *et al*. [20] have shown that particle size is an important factor for the process as the mobility of the charged particles is proportional to the size of the particles. Ferrari *et al*. [21] have also reported that the charges, hence the conductivity of the suspension, play an essential role and has an optimum value for the process. It is, nevertheless, the mechanism study of Sarkar and Nicholson [16] that has provided an insight of the colloidal process on the general charging mechanism of oxide materials. Later, Sarkar *et al*. [16, 24] and Zhang *et al*. [25] have also proposed similar kinetic models for the process, taking into account of the building of mass, and hence the electrical resistance, on the electrode or substrate.

Despite the huge amount of research effort on the process, reports on the EPD of HA as the depositing material on titanium substrates, which is one of the important areas in biomedical implant application, are thus far relatively limited. Nie *et al*. [26] and De Sena *et al*. [27] have applied EPD to deposit HA on titanium substrates and obtained a uniform thin coating with good mechanical strength. Stoch *et al*. [28] have also coated HA on titanium implants with intermediate layer of silica. Chen *et al*. [29] have coated HA and brushite on titanium using a modified ethyl alcohol aqueous electrolyte. It is noted that, nevertheless, the above mentioned works are all reporting the EPD of thin coatings of several micrometers to tenths of micrometers. In one report, Niklason [30] has reported the importance of three dimensional cellular interactions for producing cells *in vitro*. As a result, a reasonably thick coating which can accommodate better interconnected porosity structure will be desirable. However, to achieve a thicker coat of HA by EPD, Wei *et al*. [31] have reported in their work that severe cracking occurs. To overcome this cracking problem, in their subsequent works, they proposed the use of aged nano-particulate HA sols [32] and deposit with a dual coating strategy [33]. On the other hand, in their work on EPD of HA, Zhitomirsky and Gal-Or [34] have discussed on the significant effect of the suspension condition, such as particle dispersion and zeta potential, to the EPD process. From their results, it is noted that the colloidal stability of the suspension could be a main factor in the EPD process.

In the present work, to provide a systematic understanding on the colloidal processing of HA processing, the dispersion stability of the HA suspension in ethanol was investigated and characterized in terms of zeta potential, electromobility and particle size measurements as a function of suspension pH. It is noted that the condition where the suspension is most steadily dispersed is the most optimum condition for EPD. This optimum condition was hence identified from the HA suspension characterization and selected to perform the deposition. During EPD, ethanol was used as solvent in the present work so as to minimize the releasing of gas due to hydrolysis at the electrode. The present work has also shown that with appropriate colloidal properties, a uniform and uncrack coating as thick as 400 μm can be obtained through a single deposition process.

2. Experimental procedure

A modified chemical co-precipitation method was employed to prepare nanosized HA powders using calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$] and phosphoric acid (H_3PO_4) as starting materials [35]. $Ca(NO_3)_2 \cdot 4H_2O$ and H_3PO_4 were dissolved in distilled water to form a solution with calcium concentration of 0.5 M and Ca/P ratio of 1.67. After thoroughly mixing, ammonium hydroxide was poured into the solution to precipitate HA. HA powders were obtained by washing the precipitate repeatedly to remove the unwanted ions (NH_4^+ and NO_3^-) and then drying at 70 °C for 24 h.

For the preparation of the HA suspension, 3 g of HA powder was added into 100 ml of ethanol. Acid and alkaline (HNO_{3aq} and NH_{3aq}, respectively) was used to adjust the pH value of the suspension ranging from pH = 2 to pH = 9. The suspension was then taken for ultrasonic dispersion for 30 min using an ultrasonic machine (Branson Sonifier 250, USA).

The prepared suspensions of various pH values were next characterized using Acoustic Spectrometer DT-1200 to measure their zeta potential, electromobility and particle size. In general, the higher the zeta potential or electromobility, the more dispersed is the particles in the suspension. This, in turn, should give a lower particle agglomerate size in the suspension and hence corresponds a lower particle size measurement. EPD was then carried out with the HA suspension adjusted to the identified optimum condition, i.e. the highest zeta potential with lowest particle size measurement. Magnetic stirring was also employed to maintain the homogeneity of the HA particles in the suspension during EPD. It should be noted that before both characterization and deposition processes, the prepared suspensions were left to stand for 3 h to allow the reaching of suspension equilibrium. Both the characterization and EPD processes are carried out in room temperature. A titanium tube was used as the working electrode (cathode) and a cylindrical stainless steel sheet was used as the counter electrode (anode). A constant voltage of 50 V was chosen for the deposition process. The weights of HA deposited for various deposition times were also recorded. The HA coated titanium tube were then sintered at 1000 °C for 1 h in a vacuum furnace with heating and cooling rate of 5 °C/min. Microstructural examination of the deposit was then carried out using scanning electron microscope (JOEL, Japan) on the cross section of the HA deposited titanium tube. The stoichiometry of the HA before and after sintering were confirmed using X-ray diffraction (XRD 6000, Shimashu, Japan). The adhesion strength of the coating on the substrate was tested according to ASTM F1044-87 standard and the technique reported by Wei *et al*. [31]. The tests were carried out with a universal testing machine using a 10 kN loadcell and a crosshead speed of 1 mm/min. A known area portion of a stainless steel strip was first bonded onto the coating using epoxy resin. Tensile tests were then conducted by gripping one end of the stainless steel strip and the titanium substrate. The shear strength of the coating was then calculated from the fracture force over the fracture area.

3. Results and discussion

3.1. Suspension characterization

Fig. 1 shows the measurement results for zeta potential and electromobility of the HA suspension at various pH values. It can be seen that the isoelectric point (IEP) is at pH = 6.6. At this point, the zeta potential is zero. Colliding colloid particles can easily break into the electric double layer (EDL) surrounding them and coagulation may occur since the repulsive force that provide kinetic stability is at its minimum. The primary role of the EDL is to confer kinetic stability. Colliding particles break through the EDL and coalesce only if the collision is sufficiently energetic to disrupt the layers of ions and solvating molecules, or if the thermal motion has stirred away the surface accumulation of charge. This is readily happened at high temperatures, which is one

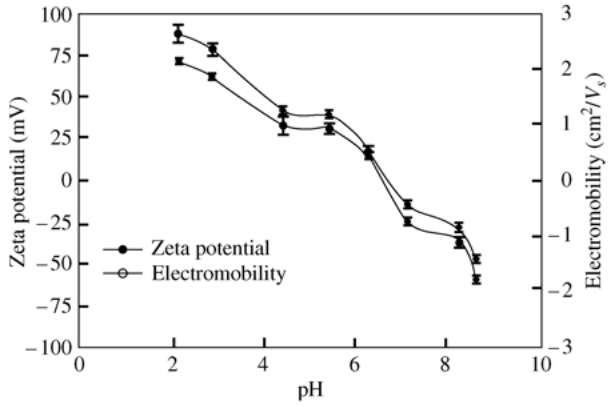

Figure 1 Zeta Potential and electromobility measurement at different pH.

reason why sols precipitate when they are heated. At isoelectric point, the zeta potential is zero and thus it offers little resistance for the colliding particle to disrupt the EDL, which in turn the colloid or suspension is usually referred to as unstable since particle agglomeration is likely to happened.

From Fig. 1, it can also be seen that the HA colloid has a high zeta potential (> 40 mV) at pH < 4 and pH > 8, which also indicates high particle mobility. However, these two regions may not necessarily offer the condition for a stable dispersed suspension. The high zeta potential values at pH < 4 and pH > 8 indicate that the surface charge of the colloid is high. Nevertheless, the high surface charge may not guarantee the resistance for particle coagulation. At high ionic concentration, the EDL shrinks and the repulsion barrier due to double layer overlap decreases. Colliding particles can approach each other at a closer distance and electrostatic attractive force may dominate over the double layer repulsive force as the repulsion barrier decreases. As a result, the zeta potential measurement alone is insufficient to provide the condition for a stable dispersed suspension. We need to utilize the result from both the zeta potential measurement and that from particle size measurement in order to determine the optimum condition for stable suspension to perform EPD.

Fig. 2 shows the particle size of the HA measured at various pH. It can be seen that the largest particle size occur at pH = 6.4. This pH is where the isoelectric point lies on as shown in Fig. 1. The results are hence consistent as at isoelectric point, large particle size is expected due to particle coagulation. On the other hand, from Fig. 1, there are two regions where high zeta potential could be obtained. These regions are pH < 4 and pH > 8. Fig. 2 has also shown that the measured particle size at these regions decreases from that measured at isoelectric point, which is desirable for EPD process. Combining the information from Figs. 1 and 2, it is noted that pH 2 provides the most stable dispersed suspension, i.e. with a high zeta potential and the smallest particle size measurement. As a result, the present EPD process was carried out with a suspension of pH value 2.

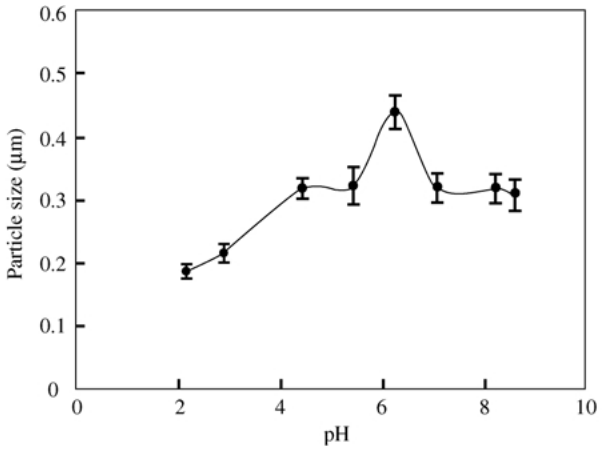

Figure 2 Particle size measurement at different pH.

3.2. Characterization of deposited weight and sintered microstructure

Fig. 3 show that the deposited mass measurement at different deposition times. It can be seen that the deposition rate reduces as the deposition time increases. This is due to the accumulation of HA particles at the titanium substrate, hence resulted in an increase of the electrical resistance. In a recent work, Zhang *et al*. [25] have provided a empirical model for the deposition process as

$$W = W_0(1 - e^{-kt}) \quad (1)$$

where W_0 is the initial weight of the powder in the suspension and k is the kinetic constant. From the experimental results presented in Fig. 3, it can be found that for the deposition of HA in ethanol, under the stable and dispersed condition, a kinetic constant of 4.5×10^{-5} provides a reasonably good estimate for the deposition mass at different deposition time.

The HA deposited titanium tubes were then sintered at 1000, 1150 and 1300 °C for 2 h. The microstructures of the HA deposits at various sintering temperatures are shown in Fig. 4. It can be seen that as sintering temperature increases, the structure becomes denser. It has been reported that an open interconnected porosity structure is advantageous as it enables penetration of the tissue and hence leads to better biointegration and mechanical stability at the interface [36, 37]. From Fig. 4, it is observed that the structure obtained from 1000 °C

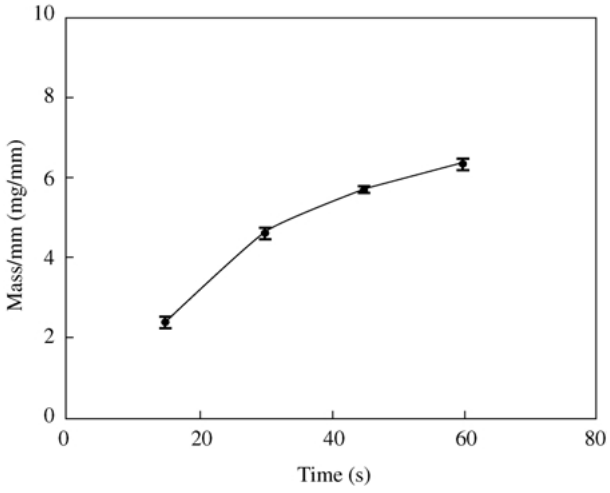

Figure 3 Deposited mass at different deposition time.

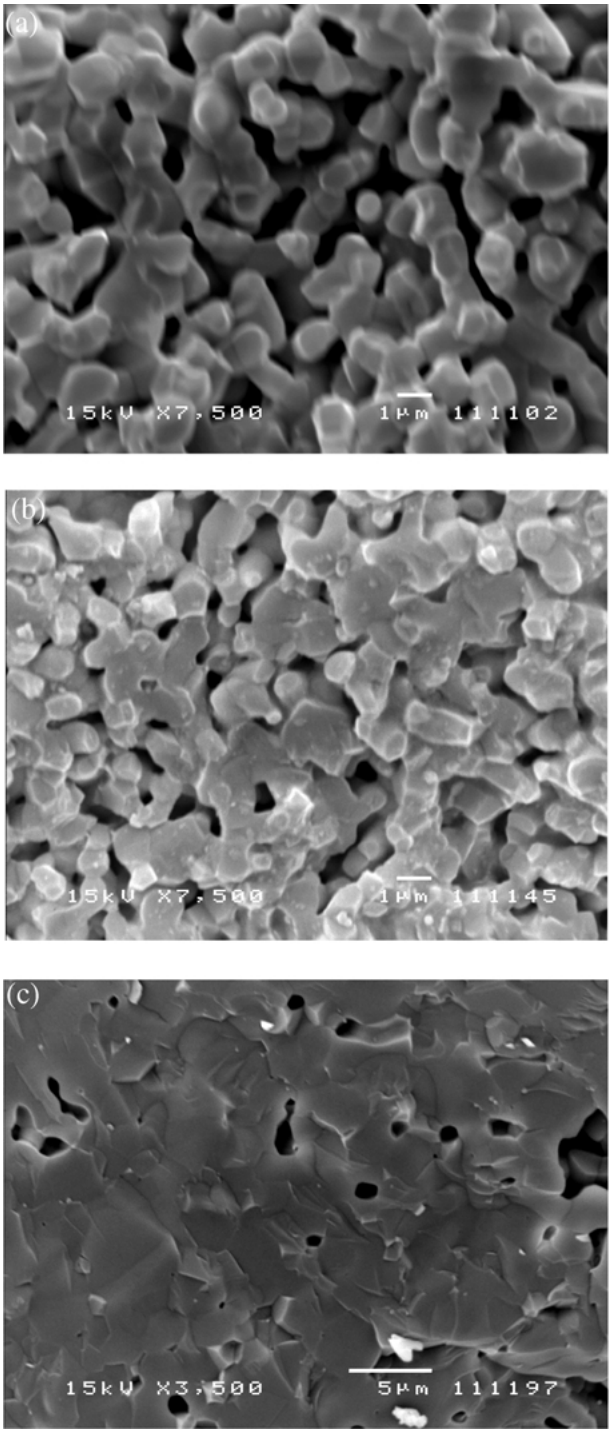

Figure 4 The microstructures of the HA deposits at various sintering temperatures; (a) 1000 °C, (b) 1150 °C and (c) 1300 °C.

sintering provides the most optimum interconnected porosity. Figs. 5 and 6 show the SEM micrograph of the cross section and the surface of the deposit respectively obtained from 1000 °C sintering. It can be seen that a layer of HA coating as thick as 400 μm has adhered very well onto the titanium substrate and no delamination or crack was observed at both the interface and surface respectively. It is hence demonstrated that with appropriate colloidal characterization, a thick uniform uncrack deposit can be produced.

It is also noted that high temperature treatment may result in the decomposition of the desirable HA structure and reduce the biocompatibility of the material [32]. The crystalline phase of the coating before and after sintering

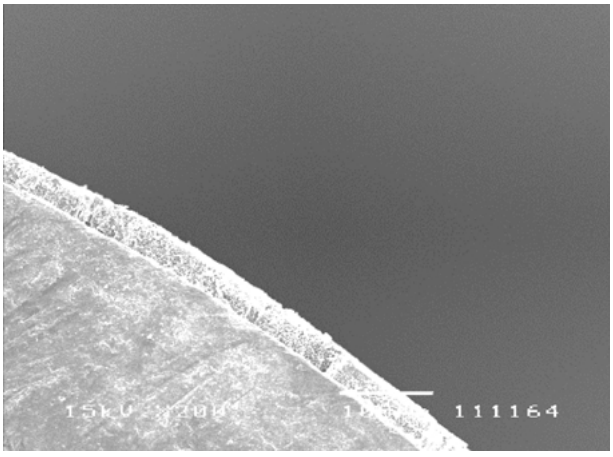

Figure 5 Cross section SEM micrograph of the EPD deposit under the identified optimum suspension condition.

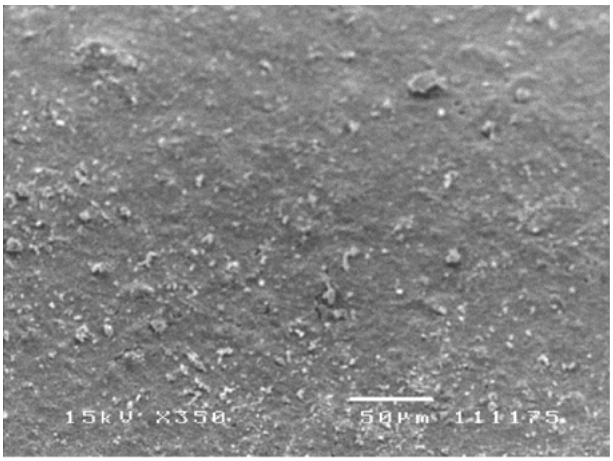

Figure 6 SEM micrograph of the uncrack deposit surface.

was examined using XRD. The XRD patterns, shown in Fig. 7, indicate that after heat treatment the main crystalline phase of the coating is still HA, together with a small amount of β-tricalcium phosphate (β-TCP) introduced from the starting powders. No new crystalline phase was observed. The diffraction peaks of HA in sintered sample become sharper and higher, indicating the coarsening of the grain after sintering. However, no obvious change for TCP, which implies that no obvious decomposition of the HA taking place during the sintering process in our experiment. Based on the coating thickness measured from the SEM micrograph, the sintered coating density of the HA deposit was estimated to be 81% of the theoretical density. The adhesion of the HA coating on the titanium substrate was quantified by shear strength test following Wei *et al*. [31] and ASTM standard F1044-87. The shear strength of the HA coating after 1000 °C sintering was measured to be 3.34 MPa. In their shear tests for HA coating on titanium, Wei *et al*. [31] have measured a shear strength of about 8 MPa. However, it should be noted that Wei *et al*. have sintered the HA to full density, compared to the 81% theoretical density of the HA in the present work. Taking the density difference into account, the present measured shear strength is found to be consistent with that reported by Wei *et al*. and has indicated good adhesion of the coating.

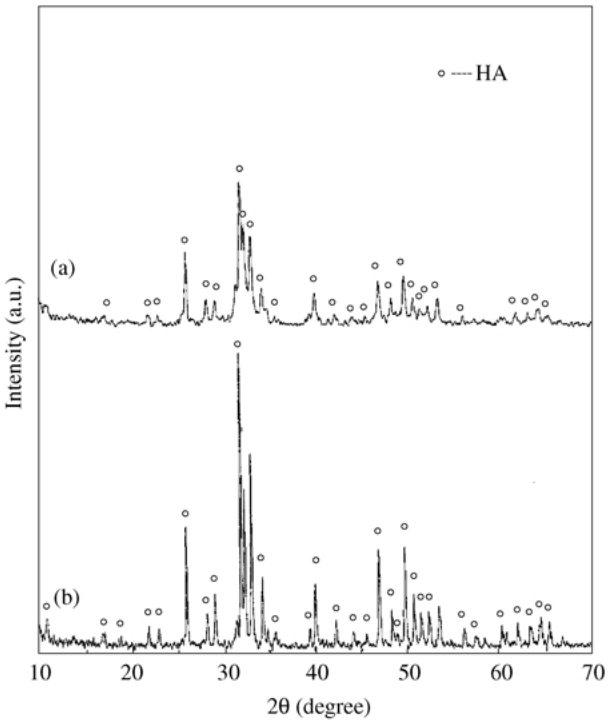

Figure 7 XRD results (a) before sintering, and (b) after sintering at 1000 °C.

4. Conclusions

HA particles were successfully deposited onto a titanium substrate via a single electrophoretic deposition process. The interfacial bonding is observed to be reasonably good from scanning electron microscopy examination and shear strength tests conducted have confirmed the good adhesion between the coating and the substrate. The deposition was also observed to be uniform and no cracks were observed. The good deposition result was attributed to the stable and dispersed HA suspension employed for the deposition process. The condition for a stable and dispersed suspension was identified through colloidal characterization on the colloid zeta potential and particle size measurement. It is noted that a high zeta potential and a small measured particle size are desired to provide a good suspension for deposition. This condition was identified to be at a pH value of 2 for HA suspension in the present work. By comparing the experimental data in the present work with theoretical model in the literature, a kinetic constant of 4.5×10^{-5} was shown to provide reasonably good estimate for the deposition mass at different deposition time using the empirical model proposed in the literature.

References

1. R. M. FRANCE, *Mater. World* **1** (2000) 19.
2. L. L. HENCH, *J. Am. Ceram. Soc.* **74** (1991) 1487.
3. H. KIDO and S. SAHA, *Proc. Biomed. Eng. Conf.* (1997) 272.
4. I. ZHITOMIRSKY, *Mater. Lett.* **42** (2000) 262.
5. W. R. LACEFIELD, P. DUCHEYNE and J. E. LEMONS, in ''Material Characteristics Versus *In Vivo* Behavior'' (New York: New York Academy of Science, 1998).
6. P. DUCHEYNE, J. CUCKLER, S. RADIN and E. NAZAR, in ''CRC Handbook of Bioactive Ceramics'', edited by J. Yamamuro, L. L. Hench and J. Wilson (CRC Press: Boca Raton, FL, 1990) p. 123.
7. M. J. FILIAGGI, N. A. COOMBS and R. M. PHILIAR, *J. Biomed. Mater. Res.* **25** (1989) 1211.
8. J. DELECRIN, S. SZMUCKLER-MONCLER, G. DACULSI, J. RIEU and B. DUQUET, in ''Bioceramics 4'', edited by W. Bonfield, G. W. Hastings and K. Tanner (Butterworth-Heinemann: Oxford, UK, 1991) p. 311.
9. J. F. KAY, in ''Handbook of Bioactive Ceramics'', edited by T. Yamamuro, L. L. Hench and J. Wilson (CRC Press: Boca Raton, FL, 1990) p. 111.
10. J. E. LEMONS, *Clin. Orthop.* **235** (1988) 220.
11. J. A. JANSEN, J. G. WOLKE, S. SWANN, J. P. VAN DER WARDEN and K. DEGROOT, *Clin. Oral Implants Res.* **4** (1993) 28.
12. M. YOSHINARI, Y. OHTSUKA and T. DERAND, *Biomaterials* **15** (1994) 529.
13. J. L. LEE and H. AOKI, *Biomed. Mater. Eng.* **5** (1995) 49.
14. P. DUCHEYNE, S. RADIN, M. HEUGHEBAERT and J. C. HEUGHEBAERT, *Biomaterials* **11** (1990) 244.
15. S. BAN and S. MARUNO, *ibid.* **16** (1995) 977.
16. P. SARKAR and P. S. NICHOLSON, *J. Am. Ceram. Soc.* **79** (1996) 1987.
17. A. FOISSY and G. ROBERT, *Am. Ceram. Bull.* **61** (1982) 251.
18. M. J. SHANE, J. B. TALBOT and R. D. SCHREIBER, C. L. ROSS, E. SLUZKY and K. R. HESSE, *J. Colloid Interface Sci.* **165** (1994) 325.
19. R. W. POWERS, *Am. Ceram. Bull.* **65** (1986) 1270.
20. K. YAMASHITA, M. MATSUDA, Y. INDA, T. UMEGAKI, M. ITO and T. OKURA, *J. Am. Ceram. Soc.* **80** (1997) 1907.
21. B. FERRARI, A. J. SANCHEZ-HERENCIA and R. MORENO, *Mater. Lett.* **35** (1998) 370.
22. H. NISHIMORI, M. TATUMISAGO and T. MINAMI, *J. Mater. Sci.* **31** (1996) 6529.
23. M. J. SHANE, J. B. TALBOT, R. D. SCHREIBER, C. L. ROSS, E. SLUZKY and K. R. HESSE, *J. Colloid Interface Sci.* **165** (1994) 334.
24. P. SARKAR, X. HUANG and P. S. NICHOLSON, *J. Am. Ceram. Soc.* **75** (1992) 2907.
25. Z. ZHANG, Y. HUANG and Z. JIANG, *ibid.* **77** (1994) 1946.
26. X. NIE, A. LEYLAND and A. MATTHEWS, *Surface & Coating Technol.* **125** (2000) 407.
27. L. A. DE SENA, M. S. SADER, A. M. ROSSI and G. A. SOARES, *Key Eng. Mater.* **218–220** (2002) 61.
28. P. S. NICHOLSON, P. SARKAR and X. HUANG, *J. Mater. Sci.* **28** (1993) 6274.
29. A. STOCH, A. BROZEK, G. KMITA, J. STOCH, W. JASTRZEBSKI and A. RAKOWSKA, *J. Molec. Struct.* **596** (2001) 191.
30. J. S. CHEN, H. Y. JUANG and M. H. HON, *J. Mater. Sci.: Mater. Med.* **9** (1998) 297.
31. M. WEI, A. J. RUYS, M. V. SWAIN, S. H. KIM, B. K. MILTHORPES and C. C. SORRELL, *ibid.* **10** (1999) 401.
32. M. WEI, A. J. RUYS, B. K. MILTHORPE and C. C. SORRELL, *J. Biomed. Mater. Res.* **45** (1999) 11.
33. M. WEI, A. J. RUYS, B. K. MILTHORPES, C. C. SORRELL and J. H. EVANS, *J. Sol–Gel Sci. Tech.* **21** (2001) 39.
34. I. ZHITOMIRSKY and L. GAL-OR, *J. Mater. Sci.: Mater. Med.* **8** (1997) 213.
35. L. B. KONG, J. MA and F. BOEY, *J. Mater. Sci.* **37** (2002) 1131.
36. H. PETITE, V. VIATEAU, W. BENSAID, A. MEUNIER, C. DE POLLAK, M. BOURGUIGNON, K. OURDINA, L. SEDEL and G. GUILLEMIN, *Nature Tech.* **18** (2000) 959.
37. P. DUCHEYNE, L. L. HENCH, A. KAHAN II, M. MARTENS, A. BURSENS and J. C. MULIER, *J. Biomed. Mater. Res.* **14** (1980) 225.

Received 19 December 2001
and accepted 6 November 2002