JTTEE5 16:588–592
DOI: 10.1007/s11666-007-9071-2
1059-9630/$19.00 © ASM International

Peer Reviewed

Durability of Titanium/Dicalcium Silicate Composite Coatings in Simulated Body Fluid

Youtao Xie, Xuebin Zheng, Xuanyong Liu, and Chuanxian Ding

(Submitted April 1, 2007; in revised form June 24, 2007)

Titanium/dicalcium silicate composite coatings with different ratios (weight ratios as Ca_2SiO_4: Ti = 3:7, 5:5, 7:3) were prepared by plasma spraying. Effects of titanium addition on coating properties, such as bonding strength, flexural modulus, and dissolution in simulated physiological environment, were studied. Results showed that the bonding strength between coating and Ti-6Al-4V substrate increased with increase of titanium content in the composite coatings. It was explained by the narrowed dissimilarity of thermal expansion coefficients between the coatings and substrates. Degradation of mechanical properties after immersion in simulated body fluid was also studied. The dissolution of dicalcium silicate in the composite coatings resulted in the decrease of flexural strength and flexural modulus of the coatings in the simulated physiological environment. The higher titanium content in the composite coatings, the stabler are the composite coatings in the physiological environment.

Keywords composite coating, durability, plasma spraying

1. Introduction

Silicon is a kind of very important trace element in the animal metabolism process and takes very important function in the early stage of bone and ligamenta tissue formation (Ref 1). Modern genetic engineering techniques demonstrate that more than 60 genes are silicon sensitive (Ref 2). Wollastonite is a raw material mainly used for traditional ceramics (Ref 3) and dicalcium silicate (Ca_2SiO_4) has been well studied because of its considerable importance in the cement and refractory industries (Ref 4, 5). These two kinds of materials are silicon-contained and composed of CaO-SiO_2 components. In our previous work, wollastonite and dicalcium silicate were plasma sprayed on titanium alloys substrates for improving the bioactivity of the implant and their good bioactivity and biocompatibility have been demonstrated (Ref 6-13). The good improved bioactivity and biocompatibility of the implants were endowed by the dissolution products of these silicate ceramics. The dissolution rate of these silicate ceramics in an aqueous solution is related to the number of the bridging oxygens. Orthosilicates hydrolyze more rapidly than other silicate species (e.g., disilicate, chain silicate) because the bridging oxygen is much more resistant to attack than nonbridging oxygen (Ref 14). Dicalcium silicate is an isolated silicate without bridging oxygen atoms and its high dissolution rate may result in the deterioration of the mechanical properties of the coatings and affect the long-term durability.

Lots of methods have been developed for improving the durability of the hydroxylapatite coatings, such as steam treatment (Ref 15), fabricating composite coatings (Ref 16), etc. For the excellent mechanical properties and corrosion resistance, good biocompatibility, titanium and its alloys are widely used in orthopedics and dentistry (Ref 17, 18). The addition of titanium in ceramic coatings is also beneficial for the preventing of cracks propagation, improvement of bonding strength and expanding coating life (Ref 19). In this article, composite coatings with added titanium particles as a second phase were fabricated for expanding the dicalcium silicate coating life. Durability of the titanium/dicalcium silicate composite coatings were evaluated in vitro by immersion in simulated body fluid (SBF) and the mechanical properties changes of the coatings were monitored.

2. Experimental

2.1 Preparation of Coatings

The dicalcium silicate (Ca_2SiO_4) powder was mechanical mixed with commercially available titanium powder as the following compositions: 30 wt.% Ca_2SiO_4 + 70 wt.% Ti (denoted by CT7), 50 wt.% Ca_2SiO_4 + 50 wt.% Ti (denoted by CT5) and 70 wt.% Ca_2SiO_4 + 30 wt.% Ti (denoted by CT3). Coatings were prepared by an atmosphere plasma spraying system (Sulzer Metco, Switzerland) with Ti-6Al-4V coupons as substrates.

2.2 Mechanical Properties Measurement

Two identical cylindrical Ti-6Al-4V rods (ϕ25.4mm× 25.4mm), one with coating (with the coating thickness about 400 μm as required by ASTM C 633 (Ref 20)) and

---

Youtao Xie, Xuebin Zheng, Xuanyong Liu, and **Chuanxian Ding,** Shanghai Institute of Ceramics, Chinese Academy, Shanghai, China. Contact e-mail: xieyoutao@mail.sic.ac.cn.

another was grit blast-roughened, were bonded together by a thin layer of glue with the tensile fracture strength over 70 MPa. Material tester (Instron-5592, SATEC, USA) was applied to measure the bonding strength between the coating and substrate at a crosshead speed of 1 mm/min. The average of five test data was given to represent the bonding strength.

Each free coating sample with dimension 25 mm (length) × 4 mm (width) × 1 mm (height) was incubated in 50 mL SBF solution at 36.5 °C. The SBF solution was refreshed every other day. The as-sprayed samples and the samples after 2, 4 weeks incubation, respectively, were applied to mechanical measurement for study of the coating durability. The SBF solution is composed with 2.5 mM of Ca^{2+}, 1.5 mM of Mg^{2+}, 142.0 mM of Na^{+}, 5.0 mM of K^{+}, 148.5 mM of Cl^{-}, 4.2 mM of HCO_3^{-}, 1.0 mM of HPO_4^{2-}, 0.5 mM of SO_4^{2-} and buffered at a pH of 7.40 with 50 mM tri (hydroxymethyl) aminomethane $(CH_2OH)_3CNH_2$) and approximately 45 mM hydrochloric acid (HCl) at 37 °C. The Tris-HCl buffer solution is composed of 50 mM tri (hydroxymethyl) aminomethane $(CH_2OH)_3CNH_2$) and buffered the pH value to be 7.40 with 45 mM hydrochloric acid (HCl)

Flexural strength of the samples was measured using a material testing instrument (Instron-5566, UK) as requirement of ASTM E-855 (Ref 21). The flexural modulus was obtained by the relationship: $E = PL^3/4bh^3\delta$, where E is the flexural modulus, P is the load, L is the span length between support, b is the specimen width, h is the specimen thickness, and δ is the deflection at midspan. Each measured value of flexural modulus represents an average of three tests. Same size of as-sprayed samples were applied for measurement of thermal expansion coefficient, which was measured by a dilatometer (402ES-3, Germany) in the temperature range of 20-600 °C.

3. Results and Discussion

3.1 Coating Characteristics and Bonding Strength

The main phases of the as-sprayed composite coatings were β-Ca_2SiO_4 and titanium (Ref 8). The coatings were built up from melted particles and had a rough surface. The cross-sectional views of these composite coatings were shown in Fig. 1. Typical lamellar structure with few pores can be seen from Fig. 1. Small cracks existed in the interface between the as-sprayed CT3 coating and substrate while no obvious cracks were found in the interface of the as-sprayed CT5 and CT7 coatings. The cracks in the interface decrease with increasing Ti content in the coatings.

Bonding strength test results of the composite coatings (about 400 μm in thickness) are shown in Fig. 2. Those of Ca_2SiO_4 and Ti coatings measured in this experiment are also illustrated. The addition of titanium to the coatings improved the bonding strength from 30.5 MPa (Ca_2SiO_4) to 49.0 MPa (CT7).

As reported by Yang et al. (Ref 22), the value of bonding strength of the coatings reflects a combination of adhesive (coating to substrate) and cohesive (within the coating layers themselves) strengths of a coating. Cohesive strength was dominated by the coating structure, i.e., crystallinity, porosity, crack formation, and lamellar texture, etc. In contrast, the adhesive strength might be affected by the coating structure, residual stress, and surface roughness of the substrate. The residual stress is closely related to the thermal expansion coefficient matching condition of the coatings and substrates. The dissimilarity of the thermal expansion coefficient between the coating and substrate induces the residual stress and therefore affects the bonding strength. Figure 3 compared

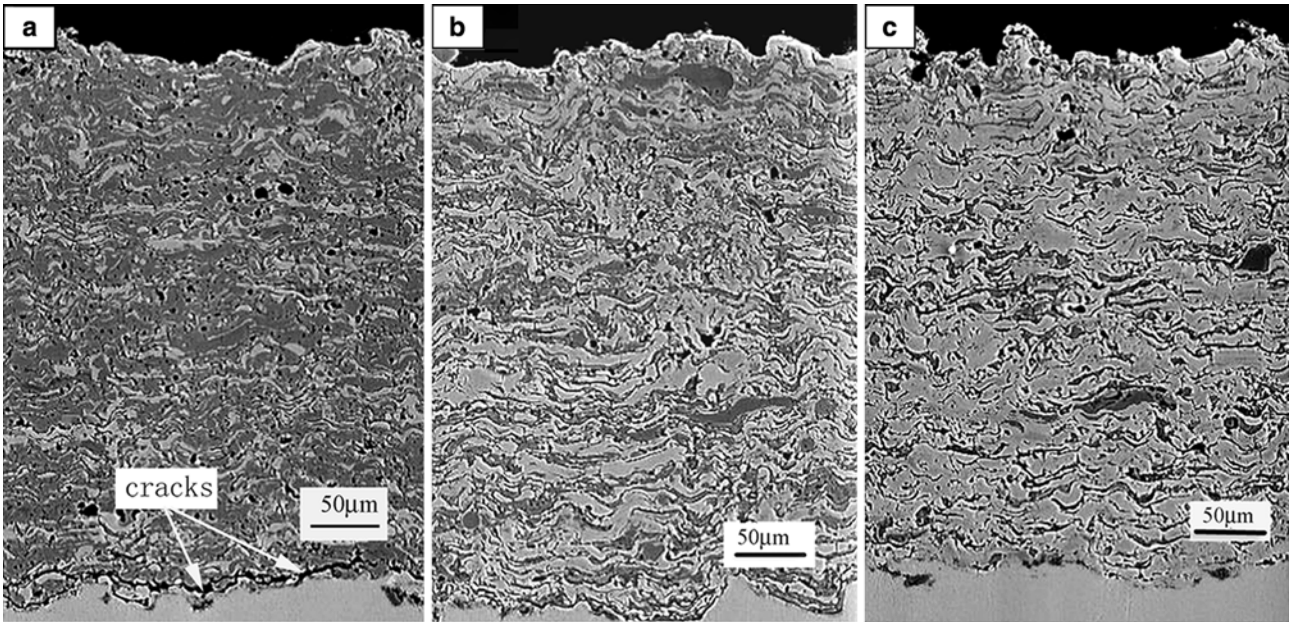

Fig. 1 Cross-sectional morphologies of the as-sprayed coatings: (a) CT3, (b) CT5, (c) CT7

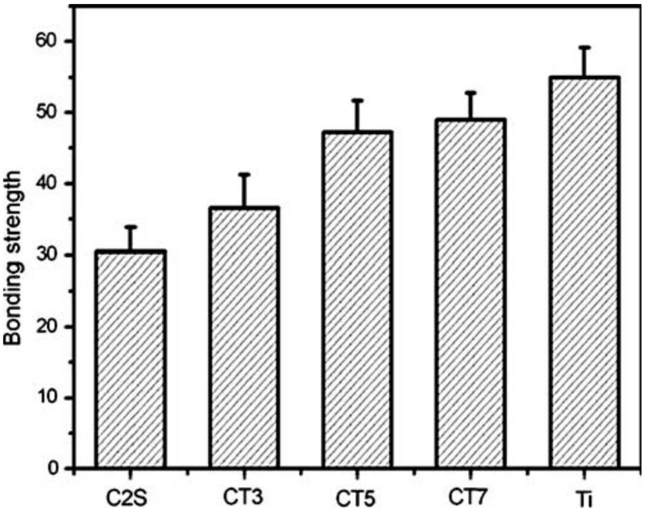

Fig. 2 Bonding strength of the composite coatings ($P < 0.05$)

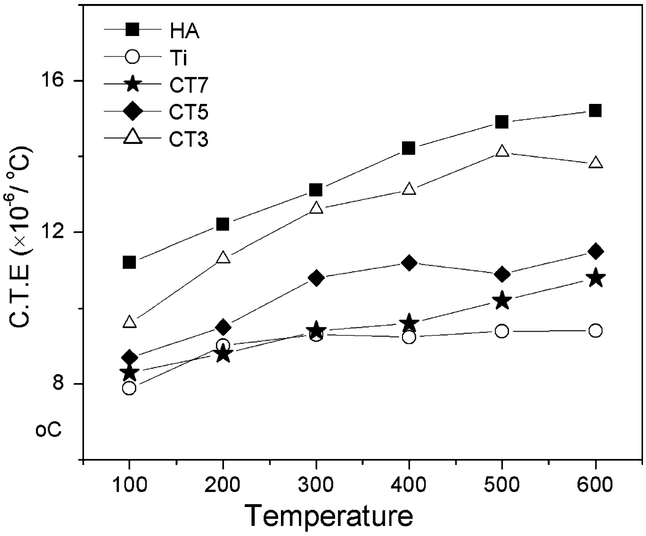

Fig. 3 Thermal expansion coefficients of the titanium/dicalcium silicate composite coatings compared with those of Ti-6Al-4V alloy (Ref 22) and HA (Ref 23)

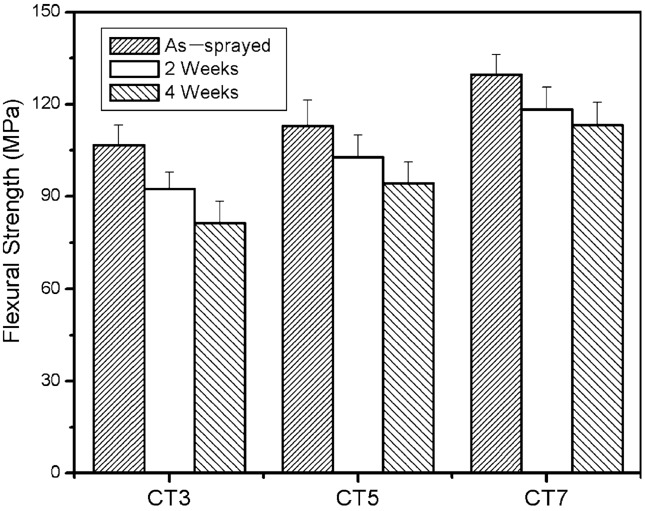

Fig. 4 Flexural strength variations of the composite coatings with immersion time in SBF ($P < 0.05$)

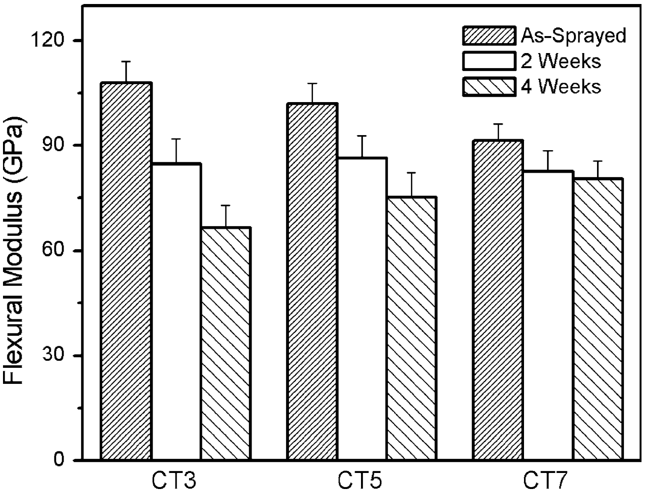

Fig. 5 Flexural modulus variations of the composite coatings with immersion time in SBF ($P < 0.05$)

the thermal expansion coefficients of the dicalcium silicate composite coatings, hydroxylapatite (HA) coating, and titanium alloy substrates. The thermal expansion coefficient of HA coating is 15.2×10^{-6}/°C (20-600 °C) (Ref 23), which is much higher than that of titanium alloy substrate (9.40×10^{-6}/°C) (Ref 24). The higher dissimilarity between the coating and substrate causes higher residual stresses during plasma spraying process and lower bonding strength (<20 MPa (Ref 25, 26)). The addition of titanium component in the composite coatings can effectively narrow down the thermal expansion coefficient dissimilarity of the coatings and substrates. With increase of the titanium contents from 30 wt.% to 70 wt.%, the thermal expansion coefficients of the composite coatings decreased from 13.8×10^{-6}/°C to 10.8×10^{-6}/°C (20-600 °C). Better adhesive condition at the coating/substrate interface can be obtained with more than 50 wt.% titanium content in the composite coatings. Apparently flaws and defects can be observed at the CT3 coating/substrate interface (as shown in Fig. 1) and therefore lower bonding strength with the substrate.

3.2 Mechanical Properties Degradation in SBF

The measured flexural strengths and flexural moduli of the composite coatings before and after immersion in SBF are shown in Fig. 4 and 5. It can be observed that with the increase of titanium components, the flexural strengths of the as-sprayed coatings increased, while the flexural moduli decreased. It may be explained by the higher flexural strength and lower flexural modulus of the titanium. Xu et al. (Ref 27) reported that the flexural modulus of

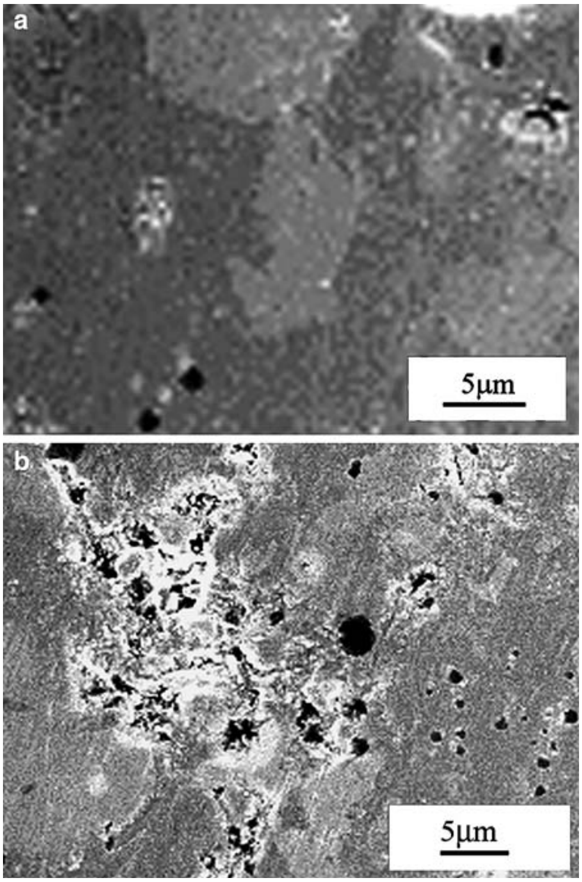

Fig. 6 Surface morphologies of the polished CT5 coating before (a) and after (b) immersion in a Tris-HCl buffer solution for 2 days

titanium is about 126.5 GPa and flexural strength is ranged from 872.2 to 891.8 MPa. While the flexural strength of the block dicalcium silicate ceramics is reported to be 97.1 ± 6.7 MPa (Ref 28) and the flexural modulus is 130 GPa (Ref 29).

With the immersion in SBF, the dissolution of dicalcium silicate component, the porosities of the coating increased and all of the flexural strengths and flexural moduli decreased. Higher dicalcium silicate content the coating contained, longer immersion time in SBF, more the flexural strengths and flexural moduli decreased. The composite coating with 70 wt.% titanium content possesses higher flexural strength, lower flexural modulus, which is much mechanical compatible with bone tissue than other coatings (Ref 30). And more, the durability of the coating with 70 wt.% titanium content is also much better than the other two composite coatings. After 4 weeks immersion in SBF, the flexural modulus only decreased 10.7%, from 91.4 ± 4.7 GPa to 80.4 ± 5.1 GPa. It indicates that the addition of titanium is beneficial to the long-term stability of the coating in the simulated physiological environment.

The degradation in the mechanical properties after SBF immersion is believed to mainly result from the dissolution of dicalcium silicate and the increased porosities in the coatings. Sergo et al. (Ref 31) reported that the mechanical properties of the coating are a function of porosity but no data were provided. Yang et al. (Ref 32) reported that there were excellent correlation between the porosity and flexural modulus of the hydroxylapatite coating. The flexural modulus decreased with the increase of porosity in the coating. We immersed a polished CT5 coating in a Tris-HCl buffer solution for 2 days, and the surface SEM morphologies were shown in Fig. 6. After immersion in the buffer solution and the dissolution of dicalcium silicate, the porosities of the coating increased obviously. In the composite coatings, the undissolved titanium component is beneficial to the maintenance of the interlamellar and interfacial bonding of the coating and consequently the durability and mechanical properties of the coatings. In fact, the results show that the higher the titanium content in the composite coatings, the more stable are the mechanical properties in a simulated physiological environment.

4. Conclusions

Titanium/dicalcium silicate composite coatings with titanium components ranging from 30 to 70 wt.% were prepared by atmospheric plasma spraying. With large amount of titanium addition, the dissimilarity of the thermal expansion coefficient between the coating and substrate was reduced. The bonding strengths of the composite coatings increase with increase of titanium content. Composite coatings with higher titanium content show smaller dissolution, and so the degree of degradation in the mechanical properties is reduced. The durability of the coatings is also enhanced.

References

1. E. Carlisle, Silicon as an Essential Trace Element in Animal Nutrition, *Silicon Biochemistry*, D. Evered and M. O'Connor et al., Eds., 1986, p 123-139
2. M. Hidebrand, D. Higgins, K. Busser, and B. Volcani, Silicon Responsive c-DNA Clone Isolated from the Marine Diatom *Cylindrotheca fusiformis*, *Gene*, 1993, **132**, p 213-215
3. V. Milan, Effect of Wollastonite Substitute in a Semivitreous Dinnerware Body, *J. Am. Ceram. Soc.*, 1956, **39**, p 323-329
4. H. Shwiete, W. Kronert, and K. Deckert, Existence Range and Stabilization of High Temperature Modification of Dicalcium Silicate, *Zement Kalk Gips*, 1968, **9**, p 359-366
5. I. Nettleship, J. Shull, and W. Kriven, Chemical Preparation and Phase Stability of Ca_2SiO_4 and Sr_2SiO_4 Powders, *J. Eur. Ceram. Soc.*, 1993, **11**, p 291-298
6. P. Valertio, M. Pereira, A. Goes, and M. Letite, The Effect of Ionic Products from Bioactive Glass Dissolution on Osteoblast Proliferation and Collagen Production, *Biomaterials*, 2004, **25**, p 2941-2948
7. P. de Aza, F. Grititan, and S. de Aza, Bioactivity of Wollastonite Ceramics: In Vitro Evaluation, *Scripta. Metall. Mater.*, 1994, **31**, p 1001-1005
8. Y. Xie, X. Liu, X. Zheng, and C. Ding, Bioactivity of Plasma Sprayed Dicalcium Silicate/Titanium Composite Coatings on Ti-6Al-4V Alloy, *Surf. Coat. Technol.*, 2005, **199**, p 105-111
9. P. de Aza, F. Guitian, and S. de Aza, Bioeutectic: A New Ceramic Material for Human Bone Replacement, *Biomaterials*, 1997, **18**, p 1285-1289

10. P. de Aza, Z. Luklinska, M. Anseau, M. Hector, F. Guitian, and S. de Aza, Reactivity of a Wollastonite–Tricalcium Phosphate Bioeutectic® Ceramic in Human Parotid Saliva, *Biomaterials*, 2000, **21**, p 1735-1741
11. P. Siriphannon, S. Hayashi, A. Yasumori, and K. Okada, Preparation and Sintering of CaSiO$_3$ from Coprecipitated Powder Using NaOH as Precipitant and its Apatite Formation in Simulated Body Fluid Solution, *J. Mater. Res.*, 1999, **14**, p 529-536
12. X. Liu and C. Ding, Apatite Formed on the Surface of Plasma-Sprayed Wollastonite Coating Immersed in Simulated Body Fluid, *Biomaterials*, 2001, **22**, p 2007-2012
13. X. Liu, S. Tao, and C. Ding, Bioactivity of Plasma Sprayed Dicalcium Silicate Coatings, *Biomaterials*, 2002, **23**, p 963-968
14. J. Oliveira, R. Correia, and M. Fernandes, Effects of Si Speciation on the *In Vitro* Bioactivity of Glasses, *Biomaterials*, 2002, **23**, p 371-379
15. H. Li, K. Khor, and P. Cheang, Effect of Steam Treatment During Plasma Spraying on the Microstructure of Hydroxylapatite Splats and Coatings, *J. Thermal. Spray. Technol.*, 2006, **15**, p 6106-616
16. C. Chu, P. Lin, Y. Dong, X. Zhu, and Z. Yin, Fabrication and Characterization of Hydroxylapatite Reinforced with 20 vol% Ti Particles for Use as Hard Tissue Replacement, *J. Mater. Sci: mater. Med.*, 2002, **13**, p 985-992
17. D. Puleo, L. Holleran, R. Doremus, and R. Bizios, Osteoblast Responses to Orthopedic Implant Materials I*n Vitro*, *J. Biomed. Mater. Res.*, 1991, **25**, p 711-715
18. D. Cohn and G. Wong, *Skeletal Research*, D. Simmons and A. Kunin, Eds., 1979, New York, p 3-20
19. J. Blum, K. Eckert, A. Schroeder, M. Petitmeret, S. Ha, and E. Wintermantel, *In Vitro* Testing of Porous Titanium Dioxide Ceramics, *Bioceramics*, T. Kokubo, T. Nakamura, and F. Miyaji, Eds., 1996, Japan, p 89-92
20. ASTM C633, Standard Method of Test for Adhesive or Cohesive Strength of Flame-Sprayed Coatings, 19th Annual Book of ASTM Standards, Part 17, ASTM, Philadelphia, PA, 1969, p 636-642
21. ASTM E-855-90, Standard Test Methods for Bend Testing of Metallic Flat Materials for Sparing Applications Involving Static Loading. West Conshohocken, PA: American Society for Testing Materials; 1990
22. Y. Yang and E. Chang, Influence of Residual Stress on Bonding Strength and Fracture of Plasma-Sprayed Hydroxylapatite Coatings on Ti–6Al–4V Substrate, *Biomaterials*, 2001, **22**, p 1827-1836
23. J. Breme, Y. Zhou, and L. Groh, Development of a Titanium Alloy Suitable for an Optimized Coating with Hydroxylapatite, *Biomaterials*, 1995, **16**, p 239-244
24. *Mechanical Engineering Handbook*, Mechanical industry press, 1996 (Beijing), p 4-46
25. K. Khor, P. Cheang, and Y. Wang, Plasma Spraying of Combustion Flame Spheroidized Hygroxylapatite (HA) Powders, *J. Therm. Spray Technol.*, 1998, **7**, p 116-121
26. K. Khor, C. Yip, and P. Cheang, Ti-6Al-4V/Hydroxylapatite Composite Coatings Prepared by Thermal Spraying Techniques, *J. Therm. Spray Technol.*, 1996, **6**, p 109-115
27. J. Xu, H. Cheung, and S. Shi, Mechanical Properties of Titanium Hydride, *J. Alloy. Compd.*, 2007, **436**, p 82-85
28. Z. Gou, J. Chang, and W. Zhai, Preparation and Characterization of Novel Bioactive Dicalcium Silicate Ceramics, *J. Eur. Ceram. Soc.*, 2005, **25**, p 1507-1514
29. J. Rodríguez, C. Baudín, and P. Pena, Relationships Between Phase Constitution and Mechanical Behavior in MgO–CaZrO$_3$–Calcium Silicate Materials, *J. Eur. Ceram. Soc.*, 2004, **24**, p 669-679
30. A. Gefen, Optimizing the Biomechanical Compatibility of Orthopedic Screws for Bone Fracture Fixation, *Med. Eng. Phys.*, 2002, **24**, p 337-347
31. V. Sergo, O. Sbaizero, R. David, and D. Clarke, Mechanical and Chemical Consequences of the Residual Stresses in Plasma Sprayed Hydroxyapatite Coatings, *Biomaterials*, 1997, **18**, p 477-482
32. Y. Yang, E. Chang, and S. Lee, Mechanical Properties and Young's Modulus of Plasmasprayed Hydroxyapatite Coating on Ti Substrate in Simulated Body Fluid, *J. Biomed. Mater. Res.*, 2003, **67A**, p 886-899