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(54) Title: Zn-RELEASEING CALCIUM PHOSPHATE (Zn-CaP) COMPOUNDS FOR ANTIBACTERIAL COATING ON ORTHODONTIC APPLIANCES AND DENTAL IMPLANTS

(57) Abstract: The invention discloses compositions of Zn-releasing calcium phosphate (Zn-CaP) compounds for use as anti-bacterial coatings for both orthodontic brackets and dental implants. These methods for providing these compositions are also disclosed. Antibacterial coatings on orthodontic brackets will minimize the problems associated with orthodontic appliance, i.e., decalcification or caries formation around and under the orthodontic appliance and calculus formation around the orthodontic appliance. When applied as anti-bacterial coatings on dental implants they minimize the incidence of peri-implantitis that often lead to implant failure and eliminate the costly process of providing a smooth section in the implant. (While roughness is necessary for better osseointegration of the implant, the same roughness facilitates bacterial adhesion and colonization). Anti-bacterial coating on roughened Ti or Ti alloy substrate will also reduce the cost of implant manufacture since applying the coating will reduce the cost of the process of polishing part of the implant to provide a smooth surface less conducive to bacterial adhesion. The invention thus benefits the patients in two areas of dentistry orthodontics and implant dentistry in terms of health and cost.
Zn-RELEASING CALCIUM PHOSPHATE (Zn-CaP) COMPOUNDS FOR ANTIBACTERIAL COATING ON ORTHODONTIC APPLIANCES AND DENTAL IMPLANTS

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Field of Invention

[0001] This invention relates to the problem associated with bacteria in using orthodontic brackets and dental implants.

Background of Invention

[0002] The orthodontic bracket is an important part of the orthodontic appliance system because it transmits the forces of the wire to the PDL tissues to effect tooth movement. It is important that the bracket be made of a material that is resistant to fracture and deformation. The bracket material of choice for many years has been stainless steel (ss), such as American Iron and Steel Institute [AISI] type I 304, because of its other many desirable qualities, such as corrosion resistance etc.) including resistance to fracture and deformation. [Odegard J, Sedner D. “Shear bond strength of metal brackets compared with a new ceramic bracket.” Am J Orthod Dentofacial Orthop 94:201-206, 1988].

Aesthetic Problems:

[0003] Because the orthodontic brackets made from stainless steel pose aesthetic problems for the patient, ceramic brackets have become the aesthetic alternative to stainless steel brackets. Ceramic brackets are aesthetic, strong, and resistant to chemical degradation. [Merrill SW et al. “Ceramic bracket bonding: a comparison of shear, tensile and torsional bond strengths of ceramic bracket.” Am J Orthod Dentofacial Orthop 106: 290-297, 1994]. However, ceramic brackets are associated with several problems such, as fracture during torsional and tipping movements, abrasion on opposing teeth, and increased frictional resistance in sliding mechanics, when compared with metal brackets. [Holt MN et al. "Fracture strength of ceramic brackets during arch wire torsion." Am J Orthod Dentofacial Orthop 99:289-293, 1991] Ceramic brackets are extremely brittle and have low fracture toughness:
even the smallest surface cracks can reduce the load required for fracture. [Garcia-Godoy F, Martin S. "Shear strength of ceramic brackets bonded to etched or unetched enamel" J Clin Ped Dent 79:181-185, 1995]. The high bond strength of ceramic brackets to enamel and their brittleness are major concerns during bracket removal, because removal may result in damage to the enamel [Kusy RP. "Morphology of polycrystalline alumina bracket and its relationship to fracture toughness and strength." Angle Ortho 58: 197-203, 1988]. Coating of the stainless steel orthodontic bracket with a white compound could solve the aesthetic problem.

**Dental caries problem:** White spot decalcification and caries on tooth surfaces in intimate contact with the orthodontic brackets are of great concern to orthodontists and their patients. Caries is an infectious disease caused primarily by *Streptococcus mutans*, a gram positive and highly acidogenic organism. These organisms multiply on specific tooth sites in the form of bacterial plaque. In susceptible individuals, they rapidly ferment carbohydrates, causing the pH to drop to a level where demineralization of enamel can occur. If this cycle is repeated, in 12 to 24 months an incipient carious lesion will develop. As more demineralization occurs, surface enamel loses its hardness, bacteria penetrate into the tooth, and frank cavitation occurs. A macroscopic cavity, then, is a relatively late stage of tooth destruction. [Goldman HS. Physician's Guide to Disease of the Oral Cavity. Oradell, New Jersey, 1982]. Coating the orthodontic brackets with a compound that would release an antibacterial agent and remineralizing agents would inhibit bacterial colonization and minimize caries formation and progression.

**Dental calculus problem:** Also sometime associated with orthodontic brackets is the formation of dental calculus. It is generally believed that bacteria play an important role in determining the nature and the extent of dental calculus formation. Dental calculus formation results from precipitation of different types of calcium phosphate salts within the organic matrix provided by bacterial plaque. [Mandel ID. "Calcium formation and prevention: An overview." Compend Contin Educ Dent Suppl 8:S235-241, 1987; Schroeder HE. Formation and Inhibition of Dental Calculus. Bern: Hans Huber, 1962]. The formation and co-existence with the organic matrix of different calcium phosphate phases (e.g., dicalcium phosphate dihydrate, DCPD, octacalcium phosphate, OCP, magnesium-substituted tricalcium phosphate, β-TCP; and carbonatehydroxyapatite, CHA) in dental calculus is due to fluctuations in the pH and composition in the oral environment and pH [LeGeros RZ, "Variations in the crystalline components of human dental calculus." J Dent Res 53:45-50, 1974; LeGeros RZ, "Calcium Phosphates in Oral Biology and Medicine." Monographs in Oral Science, Vol 15, H. Myer (ed). Basel: Karger]. Coating of the orthodontic brackets with material that would minimize mineralization of the bacterial plaque would address the calculus problem sometimes
associated with orthodontic appliances.

Dental implant problems associated with bacteria.


Anti-bacterial agents.

mouthrinses containing zinc have been shown to have the ability to inhibit plaque growth and metabolism. Compared with the topical application of fluoride, zinc has been shown to be retained in the mouth for relatively long periods, and may inhibit key sites in the metabolism of plaque bacteria involved in both caries and periodontal disease. Several clinical studies have demonstrated that zinc salts (as chloride, citrate, sulfate), ranging in concentration from 0.2 to 2.0%, alone or in combination with other antimicrobial agents (e.g. triclosan, sanguinarine or chlorhexidine), were effective in reducing calculus formation and inhibiting plaque formation [Van der Hoeven JS, et al. "The effect of chlorhexidine and zinc-triclosan mouthrinses on the production of acids in dental plaque." *Caries Res* 27:298-302, 1993; Eisenberg AD, et al. "Interactions of sanguinarine and zinc on oral streptococci and actinomyces species" *Caries Res* 25:185-190, 1991; Lobene RR, et al. "Reduced formation of supragingival calculus with use of fluoride-zinc chloride dentifrice." *J Am Dent Assoc* 77:350-32, 1987; LeGeros et al. "Dental calculus composition following use of essential oils/ZnCb mouthrinse." *Am J Dent* 76:155-160, 2002].

**Description of invention**

[0006] The present invention discloses methods for preparations and compositions of Zn-releasing calcium phosphate (Zn-CaP) compounds that can serve as an anti-bacterial coatings for orthodontic brackets and for dental implants. Depositing Zn-CaP coatings on orthodontic brackets minimizes plaque formation leading to caries formation and calculus formation. Zn-CaP coatings on dental implants minimize bacterial colonization leading to infection that cause dental implant failure and reduces the cost of implant manufacture (and the cost of the implant for the patient) by making unnecessary the process of polishing to provide a smooth surface for part of the implant.

**Preparation of Zn-releasing calcium phosphate compounds.**

[0007] The zinc (Zn) releasing calcium phosphate compounds (Zn-CaP) of the invention can be one or a mixture of the following: (a) Zn-releasing amorphous calcium phosphate (Zn-ACP), (b) Zn-releasing tricalcium phosphate (Zn-TCP), (c) Zn-releasing biphasic calcium phosphate (Zn-BCP). Preparation methods can be by precipitation (dropwise addition of solution containing calcium and zinc ions in varying Zn/Ca ratios to a solution containing phosphate or phosphate + fluoride ions or reverse addition: phosphate or phosphate + F added to (Ca+Zn) solution; or simultaneous addition Ca + Zn and phosphate solution to basic or acidic solution); hydrolysis of calcium phosphate compounds (e.g., dicalcium phosphate dihydrate (DCPD), CaHPO₄·2H₂O; dicalcium phosphate anhydrous (DCPA), CaHPO₄; octacalcium phosphate (OCP), Ca₈H₂(PO₄)₆·5H₂O; calcium phosphate monobasic, (CPM), Ca (H₂PO₄)₂·H₂O; beta-tricalcium phosphate (β-TCP), Ca₃(PO₄)₂, etc) mixed with zinc salts in solution containing carbonate or carbonate + fluoride. The reaction pH
can range from 4 to 12; reaction temperature, room temperature to 95°C. The resulting reaction products may be used as prepared or after sintering (heating) at temperatures ranging from 200 to 1200°C. Solid state reactions (e.g., reaction of Zn compound with calcium phosphate compounds) by sintering, hydrothermal or microwave method may also be used for the preparation of Zn-CaP.

[0008] The Zn-CaP preparations can also incorporate fluoride (F) or can be mixed with other simple zinc salts (chloride, sulfate, citrate) or other antimicrobial agents (sanguine, herbal extract, other ions like silver). The Zn-CaP (with or without F and other ions) can be in the form of Zn-releasing amorphous calcium phosphate (Zn-ACP), Zn-releasing apatite with low (Zn-AP) or high (Zn-AP-T) crystallinity (crystal size), Zn-releasing biphasic calcium phosphates (Zn-BCP) consisting of a mixture of Zn-AP-T and Zn-TCP (Zn-releasing tricalcium phosphate) or mixtures of Zn compounds (e.g., chloride, sulfate, citrate, phosphate) and Zn-CaP.

Preparation of Zn-releasing amorphous calcium phosphate (Zn-ACP) and Zn-releasing apatitic compound (Zn-AP) at low temperatures (room temperature) by controlled pH and calibrated agitation (stirring) and drop-rate.

[0009] Schematic representation of the reaction system is shown in appended Fig. 1. pH control is achieved using pH stat and adding NaOH solution (0.5 to 1.0M). Examples of reaction conditions and types of calcium phosphate obtained (Zn-ACP or Zn-AP) are listed in appended Table 1. Zn-ACP and Zn-AP may also be prepared by the dropwise addition of Solution A (containing calcium, Ca and Zn ions from any calcium or zinc salts. e.g., chlorides, nitrates, acetates) to Solution B (containing the phosphate ions or phosphate + fluoride ions from any sodium, ammonium or potassium phosphate or sodium, ammonium or potassium fluoride). The addition may also be reversed (Solution B added dropwise to solution A). The important parameters to obtaining Zn-ACP with varying amounts of Zn are: high pH (12 and above), high concentrations of the reactants and stirring speed (appended Table 1). Typical X-ray diffraction (XRD) patterns of Zn-ACP and Zn-AP are shown in appended Fig 2 and Fig. 3, respectively.

Preparation of Zn-releasing apatite (Zn-AP-T) and Zn-releasing biphasic calcium phosphate (Zn-BCP-T) by precipitation method (T= 37 to 100°C).

[0010] Solution A (containing calcium, Ca and Zn ions from any calcium or zinc salts, e.g., chlorides, nitrates, acetates) is added dropwise to Solution B (containing the phosphate ions or phosphate + fluoride ions from any sodium, ammonium or potassium phosphate or sodium, ammonium or potassium fluoride). The addition may also be reversed (Solution B added dropwise to Solution A) or the two solutions (Solution A and Solution B) simultaneously
added dropwise to a stirring solution of sodium, ammonium or potassium hydroxide. The reaction temperature can be maintained 37 to 100°C, and the pH can range from 5 to 12. Examples of type of Zn-CaP obtained by precipitation method from different solution Zn/Ca molar ratios are listed in appended Table 2 [LeGeros RZ et al. “Zinc effect on the in vitro formation of calcium phosphates: relevance to clinical inhibition of calculus formation.” Am J Dent 12:65-70, 1999] and illustrated in Figs. appended 4 and 5. Increasing solution Zn/Ca molar ratios promotes the formation of apatite with lower crystallinity (smaller crystal size) and formation of biphasic calcium phosphate (Zn-BCP) consisting of Zn-AP-T and Zn-TCP (appended Fig. 5)

**Preparation of Zn-AP-T and Zn-BCP-T by hydrolysis method.**

[0011] Hydrolysis of different calcium phosphates, e.g., calcium phosphate monohydrate (CPCM), Ca(H2PO4)2.H2O, dicalcium phosphate dihydrate (DCPD) CaHPO4.2H2O, or dicalcium phosphate anhydrous (DCPA), CaHPO4 with added zinc salt (chloride, carbonate, acetate) in solution containing phosphate (or phosphate + carbonate or phosphate + carbonate + fluoride) at temperature maintained at 70 to 100°C results in Zn-AP-T (Fig. 6) or Zn-BCP-T (appended Fig. 7) depending on the amount of added Zn and/or the concentration of carbonate or fluoride in the solution.

**Sintered Zn-ACP, Zn-AP, Zn-BCP.**

[0012] Sintering (heating) the products obtained by precipitation or hydrolysis at temperatures 600°C and above results in Zn-TCP or Zn-BCP (appended Fig 8).

**Demonstration of efficacy of Zn-ACP to inhibit bacterial colonization:**

**Zinc-releasing calcium phosphate compounds (Zn-ACP)**

[0013] 300mg amounts of Zn-ACP were pressed into pellets or discs at 10,000psi into pellets. Pellets were immersed in human parotid saliva for different periods (4hrs, 1 day, 4 days and 5 days) at 37°C and then examined with SEM to determine the extent of plaque formation compared to control specimens (ACP without Zn). After the period of immersion, the pellets were incubated Mueller-Hinton agar medium (composed of beef, infusion from: 300gm, casamino acids: 17.5gm, starch: 1.5gm, and agar: 17.0gm). Saliva was streaked onto the Mueller-Hinton agar plate with sterilized bacteriological loop and fixed in 3.7% formalin. After overnight incubation, bacteria in the plaque were identified from their morphology. It was observed that Zn-ACP pellets with Zn >0.12 demonstrated no bacterial colonization after 4hrs, with Zn < 0.187 after 1 day and even after 5 days exposure in human saliva at 37°C (appended Figs. 9A, 9B, appended Table 3).

[0014] Exploratory studies on the effect of electrochemically deposited ZnCl2 on rough Ti alloy substrate showed significant (p <0.01) inhibition of bacterial colonization.
(appended Fig. 10 and Fig 11) [Ansilmi AY, MS Thesis, New York University, 2001; Ansilmi AY, LeGeros JR, J Dent Res 82: abstr#2112, 2003].

**In-releasing coating deposited by electrochemical deposition.**

[0015] Zn-releasing coating (zinc chloride) deposited by electrochemical deposition method was shown to inhibit colonization by S. Sanguis bacteria [Alsilm AY. The effect of zinc coating on Streptococcus Sanguis colonization of grit-blasted, non-polished titanium alloy surfaces. MS Thesis, New York University Graduate School of Arts and Sciences, 2001; Ansilmi AY, LeGeros JP, 2003] as shown in appended Figs. 8 and 9. The disadvantage of this coating is high solubility.

[0016] The present invention will deposit Zn-releasing calcium phosphate coating in the form of either Zn-ACP, Zn-AP to Zn-AP-T, Zn-TCP, Zn-BCP. Such coatings will provide a slower release of Zn for a longer period of time.

**Demonstration of Zn-ACP to inhibit calcium phosphate formation (related to calculus formation):**

[0017] Pellets of specimen materials were immersed in calcifying solution for two and five days at 37°C and then examined with SEM to determine the extent of calcification compared to control specimens (without Zn). Results demonstrated that pellets with Zn/Ca molar ratio of 0.27 inhibited calcium phosphate formation (appended Figs. 12A, 12 B, Table 4) indicating that Zn-releasing Zn-ACP can inhibit calculus formation associated with orthodontic brackets.

**Coating deposition methods.**

[0018] The Zn-CaP coating may be deposited using one or combination of the following methods: plasma-spray method, electrochemical deposition method and precipitation method.

**Plasma-spray method.** Sintered (heated) Zn-CaP preparations can be used as source for plasma spraying coating. Parameters will be adjusted to deposit the desired coating thickness. Coating composition can be determined using x-ray diffraction method [LeGeros et al. X-ray diffraction method for the quantitative characterization of calcium phosphate coatings. In: Horowitz E, Parr Je (Eds). Characterization and performance of Calcium Phosphate coatings for Implants. ASTM STP 1196. Philadelphia, 1994, pp. 33-42]. Preliminary results using unsintered Zn-ACP as a source material for plasma-spray demonstrates the feasibility of this method to apply coating on selected areas of the orthodontic bracket (appended Fig. 13).

[0019] Because of the high temperatures involved in plasma-spray method, it is expected
Electrochemical deposition method [Lin S. LeGeros RZ, LeGeros JP. "Adherent octacalcium phosphate coating on titanium alloy using modulated electrochemical deposition method." J Biomed Mater Res 66A:819-828; LeGeros et al. "Electrochemically deposited calcium phosphate coating on titanium alloy substrates." Key Engeinner Mater 284-286:247-250, 2005]. Commercially pure Titanium (Ti) or Ti alloy (Ti6Al4V) substrates or stainless brackets can be ultrasonically cleaned then grit blasted using apatitic abrasive. A pair of grit-blasted stainless brackets or a pair of grit-blasted Ti or Ti alloy squares, serving as anode and cathode, will be immersed in solution containing calcium, zinc and phosphate solutions with Zn/Ca molar ratio ranging from 0.2 to 0.6, starting pH 4 to 12, temperature room temperature to 80°C. Coating thickness (5µ or higher) will be determined by the duration of the coating. The electrochemical deposition can be carried out with the use of modulated pulse time electric fields programmed with a custom-made dual microprocessor as previously described [Lin et al 2004; LeGeros et al 2002, 2005].

Precipitation method of coating deposition.

[0020] Coating deposition by precipitation will be using a revised method reported previously [Rohanizadeh et al. "Adherent apatite coating on titanium substrate using chemical deposition." J Biomed Mater Res 72A: 428-438, 2005]. The grit-blasted stainless steel brackets or Ti or Ti alloy can be immersed in acidic solution containing calcium, zinc, phosphate (with or without F) at 37 to 60°C. If desired, the initial coating may be transformed to a more basic Zn-CaP coating by treatment with NaOH.

[0021] While the present invention has been set forth in terms of specific embodiments thereof, the instant disclosure is such that numerous variations upon the invention are now enabled to those skilled in the art, which variations yet reside within the scope of the present teaching. Accordingly, the invention is to be construed by broadly interpreting the scope and spirit of the present disclosure and claims.
Claims

1. A method for minimizing bacterial formation on dental appliances comprising depositing an antibacterial Zn releasing Zn-CaP coating on the appliance surface.

2. A method in accordance with claim 1, wherein the composition of the said Zn-CaP coating is selected from one or more numbers of the group consisting of
   (a) Zn-releasing amorphous calcium phosphate (Zn-ACP), (b) Zn-releasing tricalcium phosphate (Zn-TCP); and (c) Zn-releasing biphasic calcium phosphate (Zn-BCP).

3. A method in accordance with claim 2, wherein the Zn-CaP coating composition is prepared as a precipitate by addition of a solution containing calcium and zinc ions in selected Zn/Ca ratios to a solution containing phosphate ions.

4. A method in accordance with claim 2, wherein the Zn-CaP coating composition is prepared by precipitation from phosphate ions being added to (Ca+Zn) solution.

5. A method in accordance with claim 2, wherein the Zn-CaP coating composition is prepared as a precipitate by simultaneous addition of Ca + Zn ions and phosphate solution to basic or acidic solution.

6. A method in accordance with claim 2, wherein the Zn-CaP coating composition is prepared by hydrolysis of one or more calcium phosphate compounds selected from the group consisting of dicalcium phosphate dihydrate (DCPD), CaHPO₄·2H₂O; dicalcium phosphate anhydrous (DCPA), CaHPO₄; octacalcium phosphate (OCP), Ca₈H₂(PO₄)₄·6·5H₂O; calcium phosphate monobasic, (CPM), and Ca₆(H₂PO₄)₂·H₂O; beta-tricalcium phosphate (β-TCP), and Ca₃(PO₄)₂); said compound or compounds being mixed with zinc salts in solution containing carbonate.

7. A method in accordance with claims 3, 4, 5 or 6, wherein the reaction pH is from 4 to 12 and the reaction temperature from 18° C to 95° C.

8. A method in accordance with claims 3, 4, 5 or 6, wherein the reaction products are coated as prepared.

9. A method in accordance with claims 3, 4, 5 or 6, wherein the reaction products are sintered at 200 to 1200° C and then used as a source for plasma spraying coating.
10. A method in accordance with claim 1, wherein the Zn-CaP coating composition further incorporates F ions.

11. A method in accordance with claim 1, wherein the Zn-CaP coating is deposited as a precipitate from solution.

12. A method in accordance with claim 1, wherein the Zn-CaP coating is electrochemically deposited.


14. An appliance in accordance with claim 13, wherein the composition of the said Zn-CaP coating is selected from one or more numbers of the group consisting of
   (a) Zn-releasing amorphous calcium phosphate (Zn-ACP), (b) Zn-releasing tricalcium phosphate (Zn-TCP); and (c) Zn-releasing biphasic calcium phosphate (Zn-BCP).

15. An appliance in accordance with claim 13, wherein the appliance is a dental implant.

16. An appliance in accordance with claim 13, wherein the appliance is an orthodontic bracket.

17. An appliance in accordance with claim 13, wherein the said coating overlies a substrate selected from one or more members of the group consisting of stainless steel, titanium, and titanium alloy.

18. An appliance in accordance with claim 13, wherein the coating further includes fluoride ions.
**Fig. 1:** Schematic presentation of the reaction system for the preparation of ACP with and without Zn at room temperature. Solution A containing Ca or Ca+Zn and Solution B containing phosphate ions are added simultaneously into the reactor containing distilled H₂O. Addition of NaOH (2M) to control pH is made with pH Stat. Drop-rate is controlled by peristaltic pumps and stirring speed is controlled by a motor (M).

**Fig. 2:** X-ray diffraction pattern of zinc-containing amorphous calcium phosphate, (Zn-ACP) with Zn/Ca = 0.22

**Fig. 3:** X-ray diffraction pattern of an apatitic calcium phosphate containing zinc (Zn/Ca = 0.12).

Both precipitates were obtained using the reaction system outlined in Fig. 1 and listed in Table 1.
Fig. 4: Apatite precipitates obtained at 37°C, pH 9, without Zn (A) and with increasing solution Zn/Ca molar ratio (B,C,D). Note decreasing crystallinity (crystal size) reflected by the broadening of the diffraction peaks.

Fig. 5: Precipitates obtained at 95°C, pH 7, without Zn (A) and with increasing solution Zn/Ca molar ratios (B,C,D). Biphasic calcium phosphate (Zn-BCP) consisting of apatite and tricalcium phosphate (X) is obtained from solution Zn/Ca = 0.10 to 0.25. Condition of precipitation for Figs. 4 and 5 is by dropwise addition of solution A (Ca or Ca+Zn) to stirring solution B (phosphate).

Fig. 6: X-ray diffraction pattern of Zn-containing apatite (Zn-AP-T) obtained by hydrolysis of calcium phosphate monobasic, (CPM) CaHPO₄·2H₂O, mixed with Zn acetate in solution containing carbonate and fluoride ions. Precipitate Zn/Ca molar ratio = 0.169.

Fig. 7: X-ray diffraction pattern of Zn-containing biphasic calcium phosphate (Zn-BCP) obtained by hydrolysis of dicalcium phosphate dihydrate mixed with Zn acetate in solution containing carbonate. Precipitate Zn/Ca molar ratio = 0.346.

Reaction conditions to obtain precipitates shown in Figs. 6 and 7: temperature 95°C, pH 8, reaction time, 24hrs.
Fig.8: X-ray diffraction pattern of hydrolysis product (Fig. 6) heated at 600°C, showing Zn-BCP consisting of Zn-AP-T and Zn-TCP (*)
**Fig. 9A:** SEM of ACP pellets without Zn (A, B) and with Zn, Zn/Ca = 0.27 (C, D) showing inhibition of bacterial colonization in Zn-containing ACP.

**Fig. 9B:** Logistic regression of saliva output by SAS software. According to this equation, if Zn/Ca ratio is 0.171, the possibility that bacteria will die is 50%. If Zn/Ca ratio is 0.023, the possibility that bacteria will die is 5%.
Fig. 10: Scanning electron micrographs demonstrating the efficacy of Zn-releasing coating in inhibiting bacterial colonization of roughened (grit-blasted) Ti alloy surface. S. Sanguis was observed to form heavy colonies on the surfaces of uncoated specimens (10A) and in the fissures and grooves of the rough surface (10B). Significant inhibition of bacterial colonization was observed on the Zn-coated specimens (10C, arrows, 10D). Zn-releasing coating was deposited using electrochemical method. [Ansiliyi AY, LeGaros, J Dent Res 84: abtr no , 2003; Ansiliyi AY, MS Thesis, NYU, 2001].

Fig 11: Significant difference (p<0.01) in bacterial count (in thousands) between uncoated (B) and Zn-coated (A) Ti alloy specimens.
Fig. 12A: SEM showing surfaces of control pellets, without Zn (A,C) and Zn-ACP with Zn/Ca = 0.27 (B,D) before (A, B) and after (C, D) incubation in calcifying solution. Calcium phosphate (Ca-P) appears as white deposits in (C). Inhibition of Ca-P formation is observed in (D).

Fig. 12B: Logistic regression of calcifying solution output by SAS software. If Zn/Ca ratio is 0.175, the possibility that no calcium phosphate will form will be 50%. If Zn/Ca ratio is 0.077, the possibility that no calcium phosphate will form will be 5%.
**Fig. 13:** (13A) conventional orthodontic bracket; (13B) idealized Zn-ACP coated orthodontic bracket; (13C) actual bracket with plasma-sprayed coating using Zn-ACP as source material.