

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

26 December 2019 (26.12.2019)



(10) International Publication Number

WO 2019/245496 A2

(51) International Patent Classification:

Not classified

(21) International Application Number:

PCT/TR2019/050080

(22) International Filing Date:

08 February 2019 (08.02.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2018/01842

09 February 2018 (09.02.2018)

TR

(71) Applicant: CUMHURİYET UNIVERSİTESİ REKTÖRLÜĞÜ [TR/TR]; Cumhuriyet Üniversitesi Rektörlüğü Kampus, Sivas (TR).

(72) Inventor: GÖRLER, Oguzhan; C.U Dis Hekimligi Fakültesi Klinik Dis Hekimligi Bolumu Protetik Dis Tedavi Anabilim Dalı, Sivas (TR).

(74) Agent: CANKAYA PATENT MARKA VE DANIŞMANLIK LİMİTED SİRKETİ; Buklum Sokak 5/16, Kavaklıdere, 06680 Ankara (TR).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- without international search report and to be republished upon receipt of that report (Rule 48.2(g))
- in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE

(54) Title: A DENTAL IMPLANT MANUFACTURING METHOD

(57) Abstract: The invention is related to a dental implant manufacturing method comprising sintering the wet infrastructure materials in a single step that have been manufactured by powder metallurgy from metal powders after electrophoretically coating them with hydroxyapatite or yttrium-stabilized zirconium oxide.



WO 2019/245496 A2

A DENTAL IMPLANT MANUFACTURING METHOD

Technical Field

The invention is related to a dental implant manufacturing method comprising sintering the wet infrastructure materials in a single step that have been manufactured by powder metallurgy from metal powders after electrophoretically coating them with hydroxyapatite or yttrium-stabilized zirconium oxide.

Prior Art

Titanium dental implants have been used in dentistry and orthopedics for many years. High biocompatibility of titanium, resistance to corrosion, low coefficient of thermal expansion, success in load bearing capacity were the reasons of preference for titanium as a dental implant. Grade-4 titanium is generally used in dental implant systems which have a history of nearly 40 years. Titanium cylindrical blocks are shaped in the form of screw by being formed on a horizontal milling machine. Following this, surface roughening processes (roughening with acid, sanding and roughening with laser) are performed, the screws sterilized and after this, packaging processes are carried out.

Chinese patent CN103361702 document of the known state of the art discloses essentially an improved method for surface modification of a metal titanium dental implant. Titanium dioxide / hydroxyapatite composite coating having biological compatibility and biological activity is prepared using the multielectrode method on the surface of the dental implant. The method essentially comprises the following stages: ultrasonic cleaning of titanium dental implant having a hundred mechanical teeth with pure water, acetone and absolute ethyl alcohol and then drying it, arranging and dispersing the titanium dioxide nanotube array with consistent openings, as a buffer layer on anodic oxide layer uniformly by using a multi layered method, electrolyzing of the hydroxyapatite coating included calcium phosphate electrical precipitation solution by using the multielectrode method in order to prepare hydroxyapatite coating which is homogenously dispersed and has high purity and better biological efficiency, processing the resultant material by means of high temperature vacuum sintering.

Titanium dioxide / hydroxyapatite composite coating prepared with these process stages enable the dental implant subjected to surface modification to have a wider and longer application possibility, better binding strength and excellent biological efficiency.

US8535722B2 USA patent document of the known state of the art, discloses a biologically compatible coating which has functionally gradual calcium phosphate along its coating thickness. Preferably, a coating comprising hydroxyapatite is in particular used for implant coatings such as dental or orthopedic implants. In functionally gradual coating, crystallinity and crystalline diameter are decreased towards the outer surface of the coating in order to provide a crystalline structure near the implant surface and implant interface.

Even though titanium has favorable properties, there are some disadvantages like a 2 or 3 months waiting period to perform osseointegration, the gray color of titanium causing esthetical problems and the potential of titanium particles to spread into the lymph nodes.

In order to eliminate these disadvantages, improved dental implants with single step sintering after electrophoretically coating wet infrastructure materials manufactured from metal powder by powder metallurgy with hydroxyapatite or yttrium-stabilized zirconium oxide are needed.

Objectives of the Invention

The object of the invention is to provide a dental implant manufacturing method with single step sintering after electrophoretically coating wet infrastructure materials manufactured from metal powder by powder metallurgy with hydroxyapatite or yttrium-stabilized zirconium oxide.

Another object of the invention is to provide a dental implant manufacturing method which enables to reduce the binding time (osseointegration) of the surface implants coated with hydroxyapatite to the jawbones.

Detailed Description of the Invention

The invention is a dental manufacturing method, comprising the steps of:

- manufacturing zirconium oxide, titanium, tungsten, molybdenum, niobium and Co-Cr metal powders by means of a powder metallurgy method,

- subjecting manufactured powder to ball milling and agitation process by using polyvinyl alcohol (PVA) or ethanol which is appropriate for liquid systems, polyvinyl butyral (PVB) based polymeric binding solutions which are appropriate for organic solvents such as 2-propanal and methylethylketone,
- 5 - removing water or organic solvents included inside the titanium and binding solution mixture following the milling process and drying the powder,
- consolidating the dried powder mixture by taking a sufficient amount primarily via hydraulic pressing under 20 MPa pressure,
- obtaining wet (green) samples by pressing, via cold isostatic pressing under 200 MPa
10 pressure of the samples that have been pressed after they have been placed inside preservative latex by vacuuming
- performing electrophoretic coating on wet samples,
- electrophoretically sintering coated wet samples.

The invention comprises manufacturing of metal powders which will improve mechanical
15 properties such as zirconium oxide, titanium, tungsten, molybdenum, niobium, Co-Cr to be used as dental implant materials via the powder metallurgy method.

In this context, to ball milling and agitation is carried out by using tungsten, molybdenum, niobium, zirconium oxide, pure titanium, co-cr metal powder with corresponding powder
20 characteristics; polyvinyl alcohol (PVA) or ethanol which is appropriate for liquid systems, polyvinyl butyral (PVB) based polymeric binding solutions which are appropriate for organic solvents such as 2-propanal, methylethylketone.

Polymeric binders were added in an amount that equals to 2-5% of the powder weight. This procedure was performed for 24 hours in high density polyethylene Nalgene containers, using yttrium stabilized tetragonal (YSZ) balls having diameters of 3 and 5 mm, that filled up half
25 of the container volume. The powder was dried by removing water and organic solvents in titanium and binder solution after grinding by using a heated magnetic mixer. Drying was performed by continuously stirring the mixture in a glass beaker via a Teflon coated magnetic stirring rod.

The powder was later filtered through a mesh having pores of 90 microns. Firstly, a sufficient
30 amount of the dried powder mixture was taken and it was consolidated in steel molds via a hydraulic pressing machine under 20 MPa pressure. Then, the pressed samples that have been

placed in preservative latex by vacuuming was pressed under 200 MPa pressure by means of cold isostatic pressing in order to obtain wet (green) samples.

Subsequently, electrophoretic coating was produced on this substrate material with a power source and an ultrasonic homogenizer. For producing electrophoretic coating, powder particles inside at submicron levels, of hydroxyapatite and yttrium stabilized tetragonal (YSZ) have been suspended inside appropriate electrolytes (ethanol and acetyl acetone).

Besides hydroxyapatite and YSZ, hydroxyapatite and YSZ based powders supplemented with strontium (Sr (max 10%)) and magnesium (Mg (max 10%)) were added into electrolyte in order to produce the coatings.

Acetylacetone was used as an electrolyte for YSZ based coatings. The electrolyte was prepared by adding 30g/L YSZ powder. On the other hand, in hydroxyapatite based studies, ethanol was used as electrolyte. The suspension was prepared by adding hydroxyapatite powder prepared with sol-gel method to ethanol electrolyte. Samples were coated by applying voltage in the range of 20-50V to the electrolytes. Sintering process was performed after designing a sintering procedure under optimum sintering conditions.

By means of the dental implant obtained according to the developed method:

- A more aesthetic look with regard to previous applications will be obtained.
- By coating the metal surface, the possibility of metal particles to accumulate in tissues will be reduced.
- The compatibility between surface coating materials and bone tissue will be utilized.
- The waiting period of 3 months that is required for osseointegration will be reduced.
- An implant in the form of a tooth root will be produced in order to obtain a product that can be used across globally.

CLAIMS

1. A dental implant manufacturing method, comprising the steps of:

- manufacturing zirconium oxide, titanium, tungsten, molybdenum, niobium and Co-Cr metal powders by powder metallurgy method,
- mixing and grinding the manufactured powders using polyvinyl butyral (PVB) based polymeric binder solutions in a ball mill,
- drying the powder by removing water and organic solvents in the mixture by means of a heated magnetic mixer,
- consolidating the dried powder mixture by means of hydraulic pressing,

characterized by comprising the steps of

- obtaining wet (green) samples by means of cold isostatic pressing of the pressed samples that have been placed in preservative latex by vacuuming,
- performing electrophoretic coating onto wet samples,
- sintering the electrophoretically coated wet samples.

2. A dental implant manufacturing method according to claim 1, **characterized by** consolidating the mixture by means of hydraulic pressing under 20 MPa pressure.

3. A dental implant manufacturing method according to claim 1 or 2 **characterized by** obtaining wet (green) samples by means of cold isostatic pressing under 20 MPa pressure, of the pressed samples that have been placed in preservative latex by vacuuming.

4. A dental implant manufacturing method according to any of the preceding claims, **characterized by** drying the mixture by continuously stirring it in a glass beaker by means of a Teflon coated magnetic stirring rod.

5. A dental implant manufacturing method according to any of preceding claims, **characterized by** producing electrophoretic coatings, by suspending hydroxyapatite and yttrium stabilized tetragonal (YSZ) powder particles at submicron levels, inside electrolytes.

6. A dental implant manufacturing method according to claim 5, **characterized in that the hydroxyapatite** and yttrium stabilized tetragonal (YSZ) powder particles comprise strontium or magnesium.

5 7. A dental implant manufacturing method according to claim 5 or 6, **characterized by** using acetyl acetone as an electrolyte for YSZ based coatings.

8. A dental implant manufacturing method according to claim 5, **characterized by** using ethanol as an electrolyte for hydroxyapatite based coatings.

10