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A process for treating the surface of articles made of titanium and alloys thereof

Verfahren zur Oberflächenbehandlung von Werkstücken aus Titan und Titanlegierungen

Procédé pour le traitement de surface de pièces en titane et en alliage de titane

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Proprietor: Morena, Italo
10139 Torino (IT)

Inventor: Morena, Italo
10139 Torino (IT)

Representative: Robba, Pierpaolo et al
Interpatent,
Via Caboto 35
10129 Torino (IT)

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Description

[0001] The present invention relates to a process for treating under a controlled atmosphere the surface of pieces or articles made of titanium and alloys thereof or similar metals. The articles are preferably formed through lost-wax casting, particularly for use in prosthodontic dentistry, orthodontics and the like.

[0002] It is well known that titanium has peculiar properties such as the affinity with O\textsubscript{2} and H, and becomes easily oxidized at high temperature regardless of the O\textsubscript{2} partial pressure.

[0003] Therefore the casting using the conventional lost wax method requires to operate under a neutral atmosphere (of argon or other noble gases).

[0004] Today there are marketed automatic apparatuses equipped with an electric arc for melting the material and adapted to pour the molten titanium into a casting cylinder under a neutral atmosphere, such as an inert gas.

[0005] These apparatuses are satisfactory but their diffusion is rather limited because of the plant high costs and the (currently) limited request since at present the specialized workshops only supplies "passivated" pieces, i.e. pieces that have been subjected to a passivation surface treatment that is completely inadequate.

[0006] In fact such a passivation is decisely questionable from an aesthetic viewpoint since it imparts a dark and dull greysh appearance to the article; as a matter of fact it involves a deep oxidation that is without aesthetic quality.

[0007] The poor biocompatibility of gold and alloys thereof, as well as that of Cr, Co, Ag and Ga alloys, and other metals presently used in the prosthetic devices and in devices for correcting defects to be used in the oral cavity has been strongly objected.

[0008] It is therefore desirable to provide the medical operators with viable alternatives to the use of gold, chromium-cobalt and also the so called "surgical" steel that until today has accounted for most of the materials used in the field of dental prosthesis, orthodontic correction and implantation under the periosteum.

[0009] As already mentioned there are known apparatuses for casting titanium articles under a neutral atmosphere by using an electric arc for melting the material and using zirconium oxide as a coating of the casting cylinder. Although the results are generally acceptable, such known process is carried out after the melting and with the cylinder full of molten metal which is not recommendable. The temperature of the cylinder is high, about 800°C, and it is not convenient to open the melting and casting machine to extract the cylinder and drop it into water, thus renouncing to the controlled atmosphere. This way one achieves a quenching of the metal with a simultaneous (deep or superficial) oxidation of the article, and a strong hydrogen contamination, which renders the article brittle and causes the formation of surface oxides of a dark grey color that are aesthetically very unpleasant (passivation).


[0012] GB 2 244 019 and GB 2 244 019 disclose a method for casting of dental metals with a casting apparatus comprising an hermetically sealed casting chamber under inert gas atmosphere.

[0013] FR 2695581 discloses a treatment of an oxidation-sensitive metal carried out in isolated surroundings. It consists of introducing the metal into these surroundings, producing a partial vacuum, melting the metal, introducing the melt into a mould, and letting it solidify. The surroundings, after they have been set under a partial vacuum, are flushed by means of an inert gas.

[0014] An example of an apparatus for casting of metals such as titanium and alloys thereof is disclosed in GB 732298.

[0015] It is the object of the present invention to overcome the above drawbacks by providing an improved process for the surface treatment of articles made of titanium and alloys thereof.

[0016] This object is achieved through a process as claimed in claim 1.

[0017] According to the invention all the operations required to obtain a finished article are accomplished under a neutral and controlled atmosphere in a single apparatus so as to obtain a finished piece that is protected by a strongly adhering film and has a fine appearance before being transferred to a normal atmosphere and then in the oral cavity environment.

[0018] The piece is then subjected to anodic oxidation or nitriding in an ammonia atmosphere, which allows the properly forming of a protective coating of oxide or nitride having an adherence strength to the piece in the order of 1,400 kg/mm\textsuperscript{2}.

[0019] The process of the invention will now be disclosed in detail with particular reference to the attached drawing showing a block diagram of an apparatus adapted to carry out the process.

[0020] Such apparatus substantially comprises a sealed vessel 1 provided with a transparent cover so that all the operating steps can be visually checked and controlled, and provided with introflexed rubber gloves for manipulating the articles.

[0021] The apparatus is further provided with a bottle of an inert gas and an associated pressure reducing valve; it is further provided with a vacuum pump and a Getter device 3 adapted to cause a quick and complete oxidation of the metal contained within the apparatus, thus removing all the residual O\textsubscript{2} molecules within the sealed vessel 1.
The sealed vessel 1 further houses a high temperature cylinder 5 where the article is cast, a tank 7 containing a liquid bath (e.g. oil) in which the article can be quenched, and an arm 6 for removing the article from the cylinder 5 and dipping it into the oil bath of the tank 7 where it is quenched in absence of contaminants.

Within the vessel 1 of the apparatus there are further provided a finishing station 9 (cooling area), a sandblasting station 11 and a pickling station 13.

Although the risk of contaminating the quenched article is very small, nevertheless according to the invention all the subsequent steps of finishing (9), sandblasting (11) and pickling (13) are accomplished under the neutral environment provided in vessel 1.

Within the vessel 1 there are contained an additional (if required) station 15 for mechanically polishing the article, a station 17 for (micro) welding operations and a station (not shown) for spot-welding operations. All the above mentioned operations of polishing and welding are carried out in the neutral atmosphere.

The vessel 1 further contains an anodic oxidation device 19 an a device 21 for nitriding the article in an ammonia atmosphere. Through these operations either an oxide coating or a nitride coating is formed on the surface of the article 23 or 25, such a coating having an adhesion force (cohesion) comprised between 1,000 kg/mm² and 2,000 kg/mm², and preferably in the order of 1,400 kg/mm². After such treatment(s), the article 23 (or 25) can be exposed to the atmosphere or to contaminants without the risk of being subjected to further undesired chemical or chemical-physical reactions, either on the surface or in the body of the article. This way the article can maintain indefinitely the aesthetic appearance that render such article preferable to those made from other materials or through a different process. Such qualities are for example a pink coloring when the article has to blend with the gengival mucosa or a milk coloring when the orthodontic devices are located on the enamel of natural dental crowns.

Claims

1. A process for obtaining prosthetic devices in titanium or alloys thereof to be used in the oral cavity, said process comprising the steps of:
   - providing a sealed vessel;
   - obtaining a neutral atmosphere in said sealed vessel by means of an inert gas, a vacuum pump and a Getter device, said Getter device comprising a metal adapted to cause a quick and complete oxidation thus removing substantially all the residual O₂ molecules within the sealed vessel;
   - forming a prosthetic device in a high temperature casting cylinder in said sealed vessel under the neutral atmosphere so obtained;
   - dipping said cast device into a quenching bath in said sealed vessel under the same neutral atmosphere, thereby provoking the quenching of the cast device in said sealed vessel under the same neutral atmosphere;
   - subsequently subjecting said cast device to anodic oxidation in said sealed vessel under the same neutral atmosphere, thereby forming a protective coating on the surface of said cast device.

2. A process as claimed in claim 1, wherein said inert gas is a noble gas, preferably argon.

3. A process as claimed in claim 1, wherein said device is formed in said high temperature casting cylinder through lost wax casting.

4. A process as claimed in claim 1, wherein the temperature of said casting cylinder is of about 800°C.

5. A process as claimed in claim 1, wherein said liquid bath is an oil bath.

6. A process as claimed in claim 1, wherein such coating has an adhesion force (cohesion) comprised between 1000 kg/mm² and 2000 kg/mm², and preferably in the order of 1400 kg/mm².

7. A process as claimed in claim 1, wherein said process further comprises the steps of finishing, sandblasting and pickling the cast device, all these further operations being carried out in said sealed vessel under said neutral atmosphere.

8. A process as claimed in claim 1, wherein said process further comprises the steps of polishing and/or welding the cast device, all these further operations being carried out in said sealed vessel under said neutral atmosphere.

Patentansprüche

1. Verfahren zur Herstellung von prothetischen Vorrichtungen, aus Titan oder Legierungen davon, zur Verwendung in der Mundhöhle, wobei das Verfahren die Schritte aufweist
   - Bereitstellen eines abgedichteten Behälters,
   - Erhalten einer neutralen Atmosphäre in dem abgedichteten Behälter mittels eines Inertgasen, einer Vakuumpumpe und einer Gettervorrichtung, wobei die Gettervorrichtung ein Metall für das Herbeiführen einer schnellen und vollständigen Oxidation aufweist, um so im wesentlichen alle restlichen O₂-Moleküle in dem abgedichteten Behälter zu entfernen,
- Ausbilden einer prothetischen Vorrichtung in einem Hochtemperatur-Gießzylinder in dem abgedichteten Behälter unter der so erhaltenen neutralen Atmosphäre,
- Eintauchen der gegossenen Vorrichtung in ein Abschreckbad in dem abgedichteten Behälter unter der gleichen neutralen Atmosphäre, wodurch das Abschrecken der gegossenen Vorrichtung in dem abgedichteten Behälter unter der gleichen neutralen Atmosphäre herbeigeführt wird, und
- darauffolgendes Unterwerfen der gegossenen Vorrichtung einer anodischen Oxidation in dem gleichen Behälter unter der gleichen neutralen Atmosphäre, wodurch eine Schutzbeschichtung auf der Oberfläche der gegossenen Vorrichtung gebildet wird.

2. Verfahren nach Anspruch 1, bei welchem das Inertgas ein Edelgas, vorzugsweise Argon, ist.
3. Verfahren nach Anspruch 1, bei welchem die Vorrichtung in dem Hochtemperatur-Gießzylinder durch Wachsausschmelzgießen gebildet wird.
4. Verfahren nach Anspruch 1, bei welchem die Temperatur des Gießzylinders etwa 800 °C beträgt.
5. Verfahren nach Anspruch 1, bei welchem das Flüssigkeitsbad ein Ölbad ist.
6. Verfahren nach Anspruch 1, bei welchem die Beschichtung eine Adhäsionskraft (Kohäsion) zwischen 1000 kg/mm² und 2000 kg/mm² und vorzugsweise in der Größenordnung von 1400 kg/mm² hat.
8. Verfahren nach Anspruch 1, welches weiterhin Polier- und/oder Schweißschritte der gegossenen Vorrichtung aufweist, wobei alle diese weiteren Vorgänge in dem abgedichteten Behälter unter der neutralen Atmosphäre ausgeführt werden.

Revendications

1. Un procédé pour obtenir des appareils prothétiques en titane ou en des alliages de celui-ci pour être utilisés dans la cavité buccale, ledit procédé comprenant les étapes de :
- fournir un récipient fermé ;
- obtenir une atmosphère neutre dans ledit récipient fermé, au moyen d’un gaz inerte, d’une pompe à vide et d’un système de Getter, ledit système de Getter comprenant un métal approprié pour provoquer une oxydation rapide et totale, éliminant ainsi pratiquement toutes les molécules d’O₂ résiduelles dans ledit récipient fermé :
- former un appareil prothétique dans un cylindre de moulage à haute température dans ledit récipient fermé sous l’atmosphère neutre ainsi obtenue ;
- plonger ledit appareil de moulage dans un bain de refroidissement dans ledit récipient fermé sous la même atmosphère neutre, provoquant ainsi le refroidissement de l’appareil de moulage dans ledit récipient fermé sous la même atmosphère neutre ;
- soumettre ensuite ledit appareil de moulage à une oxydation anodique dans ledit récipient fermé sous la même atmosphère neutre, formant ainsi un revêtement protecteur sur la surface dudit appareil de moulage.
2. Un procédé selon la revendication 1, dans lequel ledit gaz inerte est un gaz rare, de préférence l’argon.
3. Un procédé selon la revendication 1, dans lequel ledit appareil est formé dans ledit cylindre de moulage à haute température par moulage à la cire perdue.
4. Un procédé selon la revendication 1, dans lequel la température dudit cylindre de moulage est de 800 °C environ.
5. Un procédé selon la revendication 1, dans lequel ledit bain liquide est un bain d’huile.
6. Un procédé selon la revendication 1, dans lequel un tel revêtement a une force d’adhésion (cohésion) comprise entre 1000 kg/mm² à 2000 kg/mm², et de préférence de l’ordre de 1400 kg/mm².
7. Un procédé selon la revendication 1, dans lequel ledit procédé comprend en outre les étapes de finition, sablage et décapage de l’appareil de moulage, toutes ces opérations supplémentaires étant réalisées dans ledit récipient fermé sous ladite atmosphère neutre.
8. Un procédé selon la revendication 1, dans lequel ledit procédé comprend en outre les étapes de polissage et/ou soudage de l’appareil de moulage, toutes ces opérations supplémentaires étant réalisées dans ledit récipient fermé, sous ladite atmosphère neutre.