

[54] **PROSTHETIC ARTICLE AND METHOD
FOR MANUFACTURE**

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[51] Int. Cl. **A61c 13/00**

[58] Field of Search 3/1.9, 1.91, 1.912, 1.913;
128/92 C, 92 CA; 32/8, 15, 2, 10 A

[56] **References Cited**

UNITED STATES PATENTS

3,466,748	9/1969	Christensen	32/10 A
3,606,615	9/1971	Rudiger	32/10 A
3,787,900	1/1974	McGee	32/10 A

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Attorney, Agent, or Firm—Warren, Rubin &
Chickering

[57] **ABSTRACT**

There is disclosed a prosthetic article formed of an alloy containing 12–20 percent chromium; 7–12 percent cobalt; 1.5–5 percent of at least one of molybdenum, tungsten, columbium, and tantalum; 5–9 percent of at least one aluminum and titanium; 0.05–0.2 percent carbon; 0.005–0.1 percent boron; 0.05–0.2 percent of at least one of zirconium and hafnium; and the balance nickel, which may receive a strongly bonded, fused, inorganic oxide coating; and a method for manufacturing the article which includes melting the alloy in air, forming the prosthetic device, coating at least part of its surface with a coating capable of forming a fused inorganic oxide and then firing the coated article to fuse the inorganic oxide.

13 Claims, No Drawings

PROSTHETIC ARTICLE AND METHOD FOR MANUFACTURE

BACKGROUND OF INVENTION

Prosthetic devices, particularly those used in dental work, must be strong, corrosion resistant, esthetically pleasing and compatible with living tissue. In addition, the prosthetic devices must be of material which can be readily formed into complicated shapes.

Metals used for dental prosthetic devices must also be capable of accepting inorganic oxide coatings such as dental porcelain. To do this, the metals must have a compatible oxide coating on their surface. A compatible oxide coating is one that forms a bond with the fused inorganic oxide coating which is applied later. Alloys used in dental prosthetic devices must also have a coefficient of thermal expansion not too different from that of the fused inorganic oxide coatings that are used in conjunction with them, otherwise the temperature cycling experienced in applying and fusing one or more layers of inorganic oxide coating would result in cracking of the coating and sloughing off if great differences in thermal expansion were experienced between the oxide and the metal.

Metals used for prosthetic devices in the past were precious metals, particularly gold. The high cost of gold due to its natural scarcity and competing uses in making jewelry unnecessarily exaggerate the cost of prosthetic devices. In addition, the low tensile strength of gold makes gold not entirely satisfactory in some respects. Although gold readily accepts a porcelain coating, it frequently requires a separate bonding layer because its natural oxide layer is not adequate in all respects for bonding porcelain. Of course, for large prosthetic devices, such as those used for restoring hip joints, the use of gold would be prohibitively expensive.

Non-precious dental alloys have been known in the past. One such alloy is an alloy that is primarily nickel and includes beryllium as a critical alloying element. This alloy is described in U.S. Pat. No. 3,749,570. Although the alloy has satisfactory physical properties, problems are encountered both in the preparation of the alloy and in the preparation of devices from it because of the highly toxic nature of beryllium. All processes in forming such an alloy into a suitable prosthetic device must be carried on with extreme caution so that fumes, dust, or other forms of the alloy or its compounds are not inhaled or ingested by workers. Particularly in small laboratories, such as those in individual dentist's offices, it is very difficult if not impossible to provide adequate safety measures for using such a dangerous material. Even if adequate safety equipment is available, it is difficult to insure that all workers in the laboratories are sophisticated enough to understand the hazards of working beryllium alloys and to employ the safety devices that are available.

SUMMARY OF INVENTION

This invention avoids or greatly mitigates all of the problems enumerated above. The invention includes a prosthetic device made of a non-precious alloy which forms a natural oxide coating that is not only compatible with conventional fused inorganic oxides applied to dental devices, but actually participates in the bond between the fused inorganic oxide and the metal. The expansion and contraction of the alloy with changes of temperature correspond so closely with the expansion

and contraction of the fused inorganic oxides that cracking of the fused oxides is avoided. The alloy also does not contain highly toxic materials so that it may be melted, cast, ground, and otherwise worked without special precautions to avoid toxic effects.

As used in this specification, the term prosthetic device is defined as a metal device that is attached to a living animal in direct contact with living tissue to replace a missing part or to repair a malfunctioning part. Prosthetic devices may be as simple as metal inlays to fill teeth but are usually more complex, such as caps for teeth, bridges, plates or implants in bones of legs, jaws, etc. The term fused inorganic oxide refers to a substance made of inorganic oxide having its physical form altered by being subjected to high temperature. Typically a fused inorganic oxide is glazed porcelain or a vitreous material such as those used in dental work. The term bony tissue refers to any hard bone-like tissue and includes tissue such as teeth. The term bonded is defined to mean: firmly fixed to a surface without the use of an intermediary bonding material such as organic cement.

The alloys employed in the articles of this invention are those containing from 12-20 percent chromium; from 7-12 percent cobalt; from 1.5-5 percent of at least one of molybdenum, tungsten, columbium, or tantalum; from 5-9 percent of at least one of aluminum and titanium; from 0.5-0.2 percent carbon; from 0.005-0.1 percent boron; from 0.05-0.2 percent of at least one of zirconium and hafnium; and the balance substantially nickel. The alloy is formed usually by melting in air and then casting, after which it may or may not be coated completely or partially with a fused inorganic oxide coating that is bonded to its surface. The article is shaped to conform to, and to be attached to, bony tissue of a living animal. The alloy has been found to be entirely compatible not only with the bony tissue to which it is attached but also with soft tissue with which it is in contact. For example, a cap for a tooth made from the alloy of this invention coated with porcelain can be worn comfortably indefinitely by a human being. Neither the porcelain nor the alloy reacts unfavorably with the tooth or the gums, and the alloy is corrosion resistant enough to remain uncorroded in contact with body fluids and to resist galvanic effects with different metals such as may be found within the mouth. By way of example, a person having a cap made of the alloy referred to above in his mouth along with a gold filling in a different tooth and a silver amalgam filling in still a different tooth will have no galvanic reaction set up between the cap and the other metals to destroy any of the metals or to create discomfort.

The alloy of this invention must contain the essential ingredients enumerated above; however, other ingredients may also be included within its composition. One particularly useful alloy that is commercially available contains 15-18 percent chromium, 8-11 percent cobalt, 0.75-2.2 percent molybdenum, 1.8-3 percent tungsten, 0.5-2 percent columbium, 1-3 percent tantalum, 3-4 percent aluminum, 0.1-2 percent carbon, 3-4 percent titanium, 0.01-0.05 percent boron, 0.01-0.2 percent zirconium, and the balance nickel. This alloy is described in U.S. Pat. No. 3,459,545 as an alloy suitable for turbine blades in gas turbine engines.

The alloys described above are suitable to be shaped by any of the techniques usually employed in forming prosthetic devices for alloys. Particularly for dental

prosthetic devices, the initial step in shaping an alloy involves melting it in air and casting it. The resulting cast article has a thin oxide coating which adheres tightly to the metal and is compatible with the fused inorganic oxides that are generally employed for coating such prosthetic devices. The fused inorganic oxides are primarily silicon oxide and aluminum oxide or various compounds of silicon, aluminum and oxygen. Photomicrographs of the bond between the alloys described above and such materials as dental porcelain indicate that the bond is not effected at a sharp interface between the porcelain and the metal oxide layer. Rather, the natural oxide coating on the metal merges with the fused inorganic oxide to create a deep bond that has a composition gradient from the surface of the metal to the fused inorganic oxide coating. It is speculated that this deep bond, indicating a special compatibility between the fused inorganic oxides and the metal oxide coating, is the reason for the extremely firm bond that permits the alloy of this invention to be coated with fused inorganic oxides that do not crack during temperature cycling or chip off when subjected to compressive forces or abrasion.

The fused inorganic oxides may be glazed, as dental porcelain is, or they may be porous, for example in the form of a porcelain bisque. Fused dental porcelain may be applied in several layers, as is conventional in the art. For example, the metal shaped as a prosthetic device may first be coated with an opaque layer to mask the metal, after which it is coated with a porcelain layer, and finally coated with a vitreous enamel layer to produce a natural, translucent, tooth-like appearance.

If the metal prosthetic device is to be implanted directly in bony tissue, it preferably is coated with porcelain bisque. Porcelain bisque is compatible with living tissue and is porous enough for fibrous tissue to grow into the pores thereby forming a firm connection between the bony tissue and the prosthetic device. For example, an artificial hip joint may be made so that the portion connected to the femur is coated with porcelain bisque. An alloy pin so made will not only be compatible with bone tissue but will permit fibrous bone tissue to grow in the pores of the porcelain bisque to effect a very firm connection. Those portions of dental prosthetic devices that are implanted directly in jawbones also are preferably coated with porcelain bisque.

DETAILED DESCRIPTION OF INVENTION

To better describe the process of the present invention as employed to make devices of the present invention, following is a specific example of the process employed to make such an article. The process described is one for making a cap for a damaged tooth. The cap is formed of the alloy of this invention and a portion of the exterior of the cap is coated with dental porcelain.

A wax model of the cap is prepared by conventional techniques. The wax model is surrounded with what is referred to in this art as high-heat oxy-phosphate investment, and a wax insert is appropriately placed to form a sprue. Wax is removed from the investment by heating the investment to 700°F for thirty minutes followed by a burnout for 1 hour at 1600°F. Afterwards, the investment is fixed in a conventional centrifugal casting device; and an alloy containing 16 percent chromium, 10 percent cobalt, 2 percent molybdenum, 2.5 percent tungsten, 1 percent columbium, 1.25 per-

cent tantalum, 3.5 percent aluminum, 3.5 percent titanium, 0.18 percent carbon, 0.02 percent boron, 0.1 percent zirconium, and 59.95 percent nickel is placed in a quartz crucible and melted with a torch fed with acetylene and oxygen. A gas mixture obtained by setting oxygen pressure at 10 psi and acetylene pressure at 8 psi is employed. The alloy melts at a temperature slightly higher than 2450°F as indicated by the metal in the crucible slumping. A casting flux is added when the alloy begins to slump; and when the temperature is raised slightly higher the alloy becomes very fluid and forms in the shape of a sphere in the crucible. When the alloy is highly fluid it is allowed to run from the crucible into the mold.

After solidification and cooling, the casting is removed from the mold, and it is worked on as necessary with burrs or other tools, after which it is thoroughly cleaned by sandblasting with fine sand. Copings can be dressed down to 0.1–0.2 mm, which is about half the thickness required for gold dental alloys.

Areas to be covered with porcelain are fine-ground, and other areas may be polished if desired. The castings are thoroughly scrubbed with ammonium hydroxide and dried. No degassing or acid treatment is necessary to further prepare the surfaces to receive porcelain. Conventionally used and commercially available porcelains and vitreous materials are applied and used in accordance with the manufacturer's directions. All of the commercially available porcelains for dental use are entirely compatible with the casting and, in fact, form stronger bonds than when used with the dental alloys of the prior art. After the porcelain work is completed, the porcelain is covered with a soft wax; the cap is sandblasted and polished. Using ordinary polishing techniques, the alloy will take a brilliant luster, known in the art as a high micron luster, which resists corrosion and the formation of dental plaque. The cap may then be fixed in the mouth of the patient by the known dental techniques.

What is claimed is:

1. An article comprising a solid alloy comprising from about 12–20 percent chromium, from about 7–12 percent cobalt, from about 1.5–5 percent of at least one element selected from molybdenum, tungsten, columbium and tantalum, from about 5–9 percent of at least one element selected from aluminum and titanium, from about 0.05–0.2 percent carbon, from about 0.005–0.1 percent boron, from about 0.05–0.2 percent of at least one element selected from zirconium and hafnium and the balance nickel which is shaped to conform with the shape of bony tissue of a living animal and for attachment to said bony tissue.

2. The article of claim 1 wherein said bony tissue is a tooth.

3. An article comprising a solid alloy comprising from about 12–20 percent chromium, from about 7–12 percent cobalt, from about 1.5–5 percent of at least one element selected from molybdenum, tungsten, columbium and tantalum, from about 5–9 percent of at least one element selected from aluminum and titanium, from about 0.05–0.2 percent carbon, from about 0.005–0.1 percent boron, from about 0.05–0.2 percent of at least one element selected from zirconium and hafnium and the balance nickel, having a fused inorganic oxide bonded to the surface thereof.

4. The article of claim 3 wherein said alloy consists essentially of 15–18 percent chromium, 8–11 percent

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cobalt, 0.75–2.2 percent molybdenum, 1.8–3 percent tungsten, 0.5–2 percent columbium, 1–3 percent tantalum, 3–4 percent aluminum, 0.1–0.2 percent carbon, 3–4 percent titanium with a total content of aluminum and titanium not exceeding 7.5 percent, 0.01–0.05 percent boron, 0.01–0.2 percent zirconium and the balance essentially nickel.

5. The article of claim 3 wherein said fused inorganic oxide is dental porcelain.

6. The article of claim 3 wherein said fused inorganic oxide is ceramic bisque.

7. The article of claim 3 shaped to conform with the shape of bony tissue of a living animal for attachment to said bony tissue.

8. The article of claim 7 wherein said bony tissue is a tooth.

9. A process for producing a prosthetic device comprising:

A. Forming a shaped article of an alloy comprising from about 12–20 percent chromium, from about 7–12 percent cobalt, from about 1.5–5 percent of at least one element selected from molybdenum, tungsten, columbium and tantalum, from about 5–9 percent of at least one element selected from aluminum and titanium, from about 0.05–0.2 percent carbon, from about 0.005–0.1 percent boron, from about 0.05–0.2 percent of at least one element selected from zirconium and hafnium and the balance nickel, said article being shaped for attachment to bony tissue of a living animal;

B. Covering at least a portion of the surface of said

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shaped article with inorganic oxide capable of forming a fused inorganic oxide coating at elevated temperature; and

C. Heating said shaped article covered with inorganic oxide to a temperature at which a fused inorganic oxide coating is formed.

10. The process of claim 9 wherein said alloy consists essentially of 15–18 percent chromium, 8–11 percent cobalt, 0.75–2.2 percent molybdenum, 1.8–3 percent tungsten, 0.5–2 percent columbium, 1–3 percent tantalum, 3–4 percent aluminum, 0.1–0.2 percent carbon, 3–4 percent titanium with a total content of aluminum and titanium not exceeding 7.5 percent, 0.01–0.05 percent boron, 0.01–0.2 percent zirconium and the balance essentially nickel.

11. The process of claim 9 wherein said shaped article is formed by casting.

12. The process of claim 9 wherein said prosthetic device is for use in an oral cavity.

13. A physiologically compatible prosthetic alloy consisting essentially of from about 12–20 percent chromium, from about 7–12 percent cobalt, from about 1.5–5 percent of at least one element selected from molybdenum, tungsten, columbium and tantalum, from about 5–9 percent of at least one element selected from aluminum and titanium, from about 0.05–0.2 percent carbon, from about 0.005–0.1 percent boron, from about 0.05–0.2 percent of at least one element selected from zirconium and hafnium and the balance nickel.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,896,547
DATED : July 29, 1975
INVENTOR(S) : Leonard Kulwiec

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 17, change "detnal" to read --dental--;
line 28, change "0.5-0.2" to read --0.05-0.2--;
line 67, before "alloys" correct "for" to
read --from--; and
Column 4, line 4, after "melted" correct "wit" to
read --with--.
Column 5, line 26, change "0.0050.1" to read
--0.005-0.1--.

Signed and Sealed this

second Day of December 1975

[SEAL]

Attest:

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