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3,606,615

TOOTH PROSTHESES AND SURGICAL IMPLANTS
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16 Claims

ABSTRACT OF THE DISCLOSURE

An alloy for making tooth prostheses and surgical implants. This alloy consists essentially of 5 to 15 percent chromium, 5 to 15 percent nickel, 4 to 11 percent titanium, and remainder cobalt.

BACKGROUND OF THE INVENTION

The present invention relates to alloys for tooth prostheses and surgical implants.

Metal teeth prostheses and surgical implants have been made from cobalt-chromium-molybdenum alloys. Such alloys have a high tensile strength, in the region of 90 kiloponds (pond equals the unit of force in the c.g.s. system of units) per square millimeter, while exhibiting a satisfactory elongation of 8%. They are accepted by the human body. The composition of these alloys is usually 27 to 31% chromium, 4.5 to 6.5% molybdenum, up to 1% manganese and iron, up to 0.5% carbon, tungsten and silicon, perhaps 0.5 to 4% nickel, aluminum and/or vanadium, remainder cobalt.

A similar alloy for such uses contains, besides cobalt, about 22% chromium, 20% nickel, 7% molybdenum, 3% manganese, 3.5% copper, and 0.9% beryllium. This alloy exhibits some improved technological parameters, but, because of its beryllium content, is possibly somewhat toxic.

As a rule, the above alloys are melted or poured in equipment using vacuum or protective atmospheres. The forming of the basic alloys into prostheses or implants is carried out in protective equipment to assure greater cleanliness and freedom from gas.

SUMMARY OF THE INVENTION

An object of the invention is to provide an alloy for use as tooth prostheses and surgical implants in humans and other members of the animal kingdom.

Another object is to provide such an alloy having superior strength and elongation properties.

These as well as other objects which will become apparent in the discussion that follows are achieved, according to the present invention, by the provision of an alloy consisting essentially of 5 to 15% chromium, 5 to 15% nickel, 4 to 11% titanium, and remainder cobalt.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The titanium-containing alloys of the present invention possess surprisingly superior elongation values while at the same time exhibiting high strength.

In addition to the above composition limits, the alloys

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may contain 0 to 3% molybdenum and 0 to 0.1% carbon.

The titanium content is preferably 7 to 10%, while the molybdenum content is preferably present at up to a maximum of 1.5%. The elements Si, Mn, Al and/or Fe occur as impurities in the cobalt, chromium, nickel and titanium charged to make the alloys of the present invention. The total of these impurities is preferably kept at 1% or below.

The alloys of the present invention may be melted in vacuum induction furnaces using either a vacuum of 10^{-3} to 5 mm. Hg or a protective gas atmosphere (for example, argon) at a pressure of about 1 to 300 mm. Hg. Casting of the alloys is usually done in burned ceramic molds such as used for small, fine-detail castings. It is possible to cast either many small pieces to be used as starting material for producing prostheses or to cast, for example, implants in the final shape in which they are to be used.

Conventional casting processes presently used to make metal tooth prostheses can be used with the alloys of the present invention, since the melting points of the alloys of the present invention are about 1350° C. For example, the tooth prostheses can be formed in ceramic molds using the techniques of centrifuge casting. The alloys are melted using an oxygen-acetylene flame adjusted neutrally (that is, neither oxidizing nor reducing).

Further illustrative of the invention are the following examples:

Example I

An alloy A was prepared having the following composition: 6.6% Cr, 9.9% Ni, 0.015% C, 8.0% Ti, remainder Co.

Example II

An alloy B was prepared having the following composition: 11.9% Cr, 9.0% Ni, 0.53% Mo, 0.003% C, 8.2% Ti, remainder Co.

Example III

An alloy C was prepared having the following composition: 12.1% Cr, 9.1% Ni, 1.3% Mo, 0.008% C, 8.2% Ti, remainder Co.

Example IV

An alloy D was prepared having the following composition: 6.1% Cr, 11.9% Ni, 0.043% C, 7.2% Ti, remainder Co.

Example V

An alloy E was prepared having the following composition: 6.2% Cr, 11.9% Ni, 0.036% C, 8.1% Ti, remainder Co.

Example VI

An alloy F was prepared having the following composition: 9.8% Cr, 11.9% Ni, 0.040% C, 8.1% Ti, remainder Co.

Example VII

An alloy G was prepared having the following composition: 13.6% Cr, 7.9% Ni, 0.045% C, 8.5% Ti, remainder Co.

Example VIII

An alloy H was prepared having the following composition: 12.0% Cr, 7.8% Ni, 0.53% Mo, 0.030% C, 8.4% Ti, remainder Co.

The alloys of Examples I to VIII exhibited the following properties:

Alloy:	0.2% yield strength in kiloponds/mm. ²	Tensile strength in kiloponds/mm. ²	Elongation in percent
A-----	74.7	98.0	12.7
B-----	77.5	113.5	11.4
C-----	81.5	112.2	10.0
D-----	62.5	90.0	15.6
E-----	72.1	110.8	12.8
F-----	72.0	108.0	10.0
G-----	75.7	116.0	12.4
H-----	70.8	107.0	12.2

The terms "0.2% yield strength," "tensile strength," and "elongation" are used as defined on pages 4 and 5 of "Elements of Materials Science" by Lawrence H. Van Vlack, 2nd edition, 1964, Addison-Wesley Publishing Co.

The test specimens for determining the above mechanical properties are, like the above-mentioned tooth prostheses, produced using a centrifuge casting method. The cast specimens are turned to final size and polished. They have a diameter of 2.1 to 2.6 mm. and a gage length of 25 mm. This corresponds closely to the directives of British Standard 3366:1961 entitled "Specification for Dental Cobalt Chromium Casting Alloy." The strain rate used in obtaining the 0.2% yield strength data was about 10^{-4} sec.⁻¹.

In order to test the compatibility of the prostheses and implants of the present invention with the bodies of animals and, in particular, humans, comparative corrosion and electrochemical measurements were carried out. The comparison alloys were the cobalt-chromium-molybdenum alloys described above in the Background of the Invention. These alloys have been used successfully for many years as tooth prostheses and surgical implants. The comparison alloys had the following composition: 27 to 30% Cr, 4.5 to 6.5% Mo, 0.5% C, 0.8% Si, 1% Mn, 0 to 0.5% W, up to 1% Fe, up to 1% Ni, remainder Co.

The corrosion measurements were carried out both in artificial saliva and in an aqueous solution containing 1% lactic acid and 0.25% NaCl. The solution was held at 40° C. The test specimens were left in such solution for more than one year. Even for such long test time, both the comparison alloys and the alloys of the present invention gave the extremely small corrosion velocities of 0.01 mm./year or less. Such velocities are below the accuracy of measurement of usual equipment.

Current-time curves were recorded in artificial saliva in the electrochemical measurements. Potentials of +100 and +150 mv. as measured against a saturated calomel electrode were used. These potentials can arise should the alloys of the present invention come in contact with gold in the mouth of an individual. In these experiments, both the comparison alloys and those of the present invention gave current densities of 10^{-4} to 10^{-5} milli-amperes per square centimeter. Such values are hardly measurable using conventional equipment. In no case in these experiments was evidence of corrosion found.

In addition to the above comparative experiments, tooth prostheses made from the alloys of the present invention have been in the mouths of humans now for more than one year. Neither evidence of corrosion in the prostheses nor any type of disturbance or effect on the persons involved has been noted.

The artificial saliva used for the tests described herein was an aqueous solution containing the following additions per litre;

	Grams
K ₂ HPO ₄ -----	0.95
CaCl ₂ -----	0.16
KSCN -----	0.22
NaHCO ₃ -----	0.77
NaCl -----	0.23
KCl -----	0.55
(NH ₂) ₂ CO -----	0.13

As used in the claims, the term "prosthesis" is meant to include tooth prostheses and implants within an animal serving as replacements, supplements, or reinforcements of bones, organs, tissue, etc.

5 Tooth prostheses within the meaning of the invention are metallic parts with artificial non-metallic teeth attached thereto which are introduced into the mouth of an individual for fixing the artificial teeth and taking up the forces developed, for instance, during chewing.

10 The test specimens used for determining the mechanical properties of the alloy G were manufactured in the following manner:

At first, electrolytic cobalt, electrolytic chromium and nickel mixed in proportions to obtain the desired composition of the alloy were melted in a vacuum induction furnace using a vacuum of 10^{-1} to 10^{-3} mm. Hg. After complete degassing of the metal bath, commercially pure titanium melted in a vacuum electric-arc furnace was added to the liquid alloy in the quantity required to obtain the desired composition. After complete solution of the titanium in the metal bath, the liquid alloy was cast at a temperature of about 1430° C. into a burned ceramic mold placed in a vacuum induction furnace. This burned ceramic mold had been manufactured in the conventional manner by the lost wax process. The cast alloy which after solidification was available in cylindrical form was blasted with steel shot and subsequently cut up into pieces weighing between 25 and 30 grams. For making the test specimens, these metal pieces were melted using an oxygen-acetylene flame adjusted neutrally, whereupon the liquid metal was cast centrifugally into burned ceramic molds also made by the lost wax process. Before casting, these molds were preheated to about 950° C. and the casting temperature was again about 1430° C. The solidified as-cast specimens had a diameter of 2.8 mm. When turned and polished, the test specimen had a diameter of 2.4 to 2.5 mm. and a gage length of 25 mm. The mechanical properties of the alloy G shown in the table represent the average values obtained from measurements on 4 different test specimens.

Unless indicated otherwise, all percentages given throughout this disclosure for compositions are percents by weight.

It will be understood that the above description of the present invention is susceptible to various modifications, changes and adaptations, and the same are intended to be comprehended within the meaning and range of equivalents of the appended claims.

We claim:

1. A prosthesis made of an alloy consisting essentially of, in percent by weight, 5 to 15% chromium, 5 to 15% nickel, 4 to 11% titanium, and remainder cobalt.

2. A prosthesis as defined in claim 1, said alloy containing 0 to 3 weight percent molybdenum.

3. A prosthesis as defined in claim 2, wherein the amount of molybdenum is at most 1.5% by weight.

4. A prosthesis as defined in claim 1 said alloy containing 0 to 0.1 weight percent carbon.

5. A prosthesis as defined in claim 4, said alloy containing 0 to 1.5 weight percent molybdenum.

6. A prosthesis as defined in claim 4, the alloy consisting essentially of, in percent by weight, 6.6% Cr, 9.9% Ni, 0.015% C, 8.0% Ti, and remainder Co.

7. A prosthesis as defined in claim 5, said alloy consisting essentially of, in percent by weight, 11.9% Cr, 9.0% Ni, 0.53% Mo, 0.003% C, 8.2% Ti, and remainder Co.

8. A prosthesis as defined in claim 5, said alloy consisting essentially of, in percent by weight, 12.1% Cr, 9.1% Ni, 1.3% Mo, 0.008% C, 8.2% Ti, and remainder Co.

9. A prosthesis as defined in claim 1, wherein the amount of titanium is between 7 and 10 weight percent.

10. A prosthesis as defined in claim 1, wherein, in weight percent, the amount of chromium is in the range of 6.1 to 13.6, the amount of nickel is in the range of 7.8 to 11.9, and the amount of titanium is in the range of 7.2 to 8.5.

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11. A prosthesis as defined in claim 10, said alloy containing carbon in the range of 0.003 to 0.045 weight percent.

12. A method of using an alloy consisting essentially of, in percent by weight, 5 to 15% chromium, 5 to 15% nickel, 4 to 11% titanium, and remainder cobalt, comprising plac- 5 ing said alloy as a prosthesis in the body of an animal.

13. A method as claimed in claim 12, said alloy contain- ing 0 to 3 weight percent molybdenum.

14. A method as claimed in claim 12, said alloy contain- 10 ing 0 to 0.1 weight percent carbon.

15. A method as claimed in claim 12, wherein, in weight percent, the amount of chromium is in the range of 6.1 to 13.6, the amount of nickel is in the range of 7.8 to 11.9,

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and the amount of titanium is in the range of 7.2 to 8.5.

16. A method as claimed in claim 15, said alloy containing carbon in the range of 0.003 to 0.045 weight percent.

References Cited

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ROBERT PESHOCK, Primary Examiner

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32—10A; 128—92C

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,606,615 Dated September 21st, 1971

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

In the heading of the patent, line 9, change "P 15 58 448.2" to --P 19 56 738.5--. Column 1, line 25, change "teeth" to --tooth--. Column 3, line 43, change "along" to --a long--.

Signed and sealed this 4th day of April 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents