

[54] **HIGH STRENGTH, DUCTILE  
COBALT-BASE DENTAL ALLOY**

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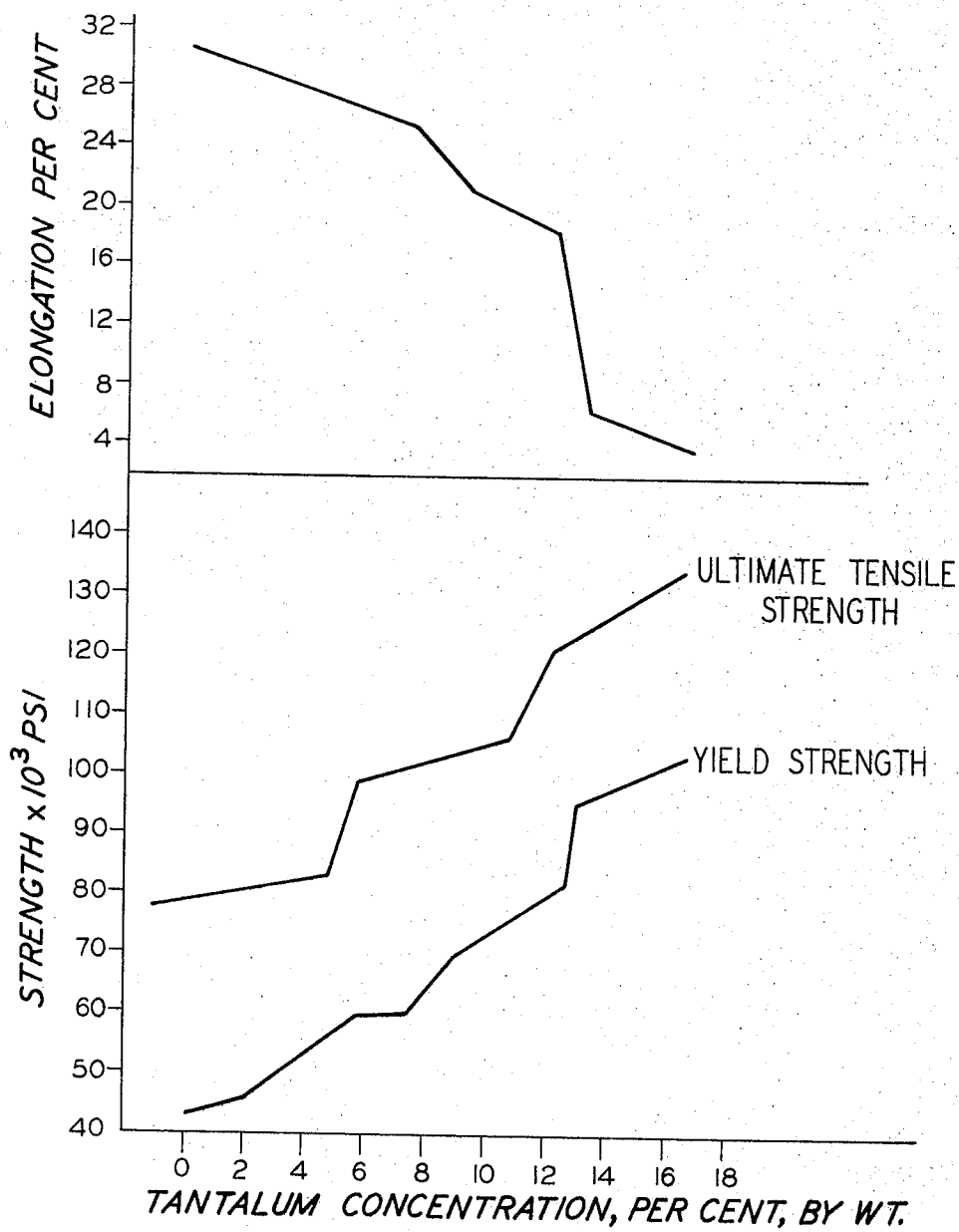
[57] **ABSTRACT**

A low-cost cobalt-base alloy system suited for dental and other biomedical appliances is essentially free of carbon and molybdenum, and has an alloy base comprising cobalt, chromium, and nickel as essential major alloying elements and a member of the group comprising tantalum and niobium alloyed therewith as the major strengthening element to produce an alloy matrix having a structure which is ductile at room temperature, has high stacking fault energy to achieve further ductility and an average low electron hole number for the complete alloy matrix to prevent the formation of embrittling phases during cooling. The alloy system utilizes coherent strengthening compounds which form an integral part of the alloy matrix. Combinations of selected percentages, by weight, of cobalt, chromium, nickel, e.g. 35–45 percent cobalt, 20–32 percent chromium, and 30–40 percent nickel, are disclosed as the alloy base and is hardened by selected percentages of strengthening elements, e.g., tantalum and niobium, which have sufficient solubility in the alloy base to produce significant solid solution hardening and combine with cobalt to form coherent precipitate particles. Modifications are also disclosed.

**6 Claims, 1 Drawing Figure**

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## HIGH STRENGTH, DUCTILE COBALT-BASE DENTAL ALLOY

This invention relates to a low cost cobalt-base alloy especially suited for dental and other biomedical appliances. More particularly, this invention is concerned with a cobalt-base dental alloy system essentially free of carbon and molybdenum, and consisting essentially of cobalt, chromium, nickel, and tantalum and/or niobium, and which possesses a combination of ductility and strength properties highly superior to presently available alloys used for the same purposes.

Alloys for dental applications should fulfill certain requirements. The alloy should be sanitary and contain no toxic ingredients. It should also be able to attain and to maintain a metallic luster and have high resistance to corrosion. The strength and hardness of the alloy should permit function and ease of fabrication, finishing, adaptation, and adjustment. The alloy should neither warp, change in dimension, nor fracture under normal masticatory loads. The overall mechanical properties of the alloy should be sufficiently high that a fairly small bulk of metal may be used in a dental appliance. The melting point of the alloy should be such that the appliance can be simply fabricated through the use of conventional dental procedures. When cast, the alloy should have no adverse reaction with the investing media so that no contamination of the alloy takes place during casting and so that it separates from the investing media to give a smooth, clean surface. The castability of the alloy and its coefficient of thermal expansion should be such that the details and exact dimensions of the appliance are reproduced. The alloy should have a sufficient level of ductility to permit necessary alterations and adjustments when inserted in the mouth of a patient and its toughness should be adequate to withstand accidental dropping without fracture. The alloy should further have minimal abrasive effects on the hard oral tissues in which it comes into contact during use and be cosmetically acceptable.

None of the dental alloys available today fulfill all of the above requirements, and it is the principal object of this invention to provide a cobalt-base alloy system which meets the requirements of alloys indicated for all casting metal dental applications.

Another object of this invention is to provide a high strength, high ductility, high corrosion resistant, body-compatible, cobalt-base alloys of suitable hardness for the production of dental and other biomedical appliances.

A still further object of this invention is the provision of an improved cobalt-base alloy essentially free of molybdenum and carbon and which is strengthened by selected metallic elements which produce an alloy matrix having a structure which is ductile at room temperature, has high stacking fault energy to achieve further ductility, and an average low electron hole number for the complete alloy matrix to prevent the formation of embrittling phases during cooling.

Another object is the provision of such an alloy having major percentages of chromium and nickel, strengthened by coherent precipitate particles of intermetallic compounds of cobalt and tantalum or niobium and which is essentially free of precipitates of carbon and molybdenum.

A further object of this invention is to provide an improved cobalt-base alloy suited for dental appliances

which is essentially free of carbon and molybdenum and is strengthened by intermetallic compounds of tantalum and/or niobium.

Still another object of this invention is the provision of a dental alloy consisting essentially of, by weight, about 40 percent cobalt, 30 percent chromium, and 30 percent nickel, which is essentially free of carbon and molybdenum, and which is strengthened by the addition of not more than about 17 percent tantalum or 10 percent niobium.

Other objects will be in part obvious and in part pointed out more in detail hereinafter.

The invention accordingly comprises the combination of elements disclosed herein and articles possessing the features, properties, and characteristics which are exemplified in the following disclosure.

In the drawing, the single FIGURE is a graph showing selected mechanical properties of certain alloys of this invention.

This invention is based on the principle that the ductility of cobalt alloys is improved by increasing the proportion of the ductile face centered cubic (FCC) structure contained in the alloy at room temperature by reducing the proportion of the less ductile hexagonal close packed (HCP) structure which is normally present in the alloy at room temperature. The above favorable transformation is effected by raising the resistance of the alloy matrix to the formation of the embrittling stacking faults in the cobalt-based alloy upon cooling. This is done by raising the stacking fault energy (SFE) of the alloy through the addition of carefully selected metallic elements.

Accordingly, in carrying out this invention, I have selected an alloy base which offers high resistance to the formation of stacking faults by balancing the adverse effect of chromium, the presence of which is necessary to offer corrosion resistance, by the addition of nickel, which has a favorable effect on SFE of the alloy, thus maintaining its ductility. Further, I have added strengthening elements carefully selected to raise the SFE of the alloy thus maintaining its ductility.

In addition, the ductility of currently available cobalt alloys is impaired by the formation of embrittling phases in the alloy. These phases may be avoided by utilizing the principle of reducing the average electron hole number of the alloy ( $\bar{N}_v$ ). The  $\bar{N}_v$  is dependent on the electron hole number ( $N_v$ ) of the elements contained as solutes in the alloy. In this regard, however, the  $N_v$  of elements which precipitate out from the alloy due to formation of various compounds during cooling of the alloy do not contribute to increasing  $\bar{N}_v$ .

As described in an article by Linus Pauling entitled "The nature of interatomic forces in metals," published in Physical Review, 54:899, 1938, in a given metallic atom, the outer most orbitals, termed the bonding orbitals, are occupied by the bonding electrons responsible for bonding the atom to its neighboring metallic atoms. At a given instant in time and on the average, the bonding orbitals are only partially occupied by the bonding electrons. Such partial occupation means that the outer orbitals are partially vacant of electrons or possess an "electron hole." The total average number of vacant orbitals in a given metallic atom is called the electron hole number of the metal ( $N_v$ ). The average electron hole number ( $\bar{N}_v$ ) is the resultant of adding all  $N_v$  for the participating elements in the alloy matrix. The higher the  $\bar{N}_v$  of a given Co-Cr-Ni alloy the higher

the chance for the precipitation of embrittling phases. The quantities of metals consumed in precipitation do not enter in calculating  $\bar{N}_r$  of the alloy matrix and hence do not participate in the formation of embrittling phases. A low  $\bar{N}_r$  may thus be obtained by either choosing elements of low  $N_r$  to form an alloy or by using elements that will react in the alloy and precipitate out from the alloy matrix.

Accordingly, in carrying out this invention, I have selected an alloy-base for the system which possesses a low  $\bar{N}_r$ , and have strengthened the alloy base by adding elements which will have minor or no effect on raising the  $\bar{N}_r$  through controlling their percentage as solutes or by eliminating their effect on  $\bar{N}_r$  by formation of compounds which precipitate out.

Further, this invention is based on the principle that coherent strengthening compounds are more efficient than incoherent compounds in improving the yield strength of the alloy. Moreover, strengthening by coherent compounds causes a slower rate of work hardening which results in stronger and more ductile alloys than strengthening by incoherent compounds such as carbides.

The strength advantage of coherent compounds is due to their fineness, greater number, and the closer center-to-center distance of their particles when compared to the much larger particles of incoherent compounds. An additional advantage resides in the fact that coherent compounds form an integral part of the alloy matrix while the larger particles of incoherent compounds act as alien particles embedded into the alloy matrix, thus disrupting its continuity and acting as points of stress concentration where fracture initiates.

The ductility advantage offered by coherent compounds is based on the dislocation theory to the effect that once the yield strength has been reached the effective distance between the coherent particles remains virtually constant while the effective distance between incoherent particles decreases. Accordingly, work hardening to the breaking point is approached in a longer period of time (more elongation) when the strengthening compound is coherent.

In order to develop a suitable dental alloy, a cobalt base alloy was selected since the human body acts favorably to cobalt as demonstrated by successful experience of cobalt-base implants.

However, while cobalt has a face centered cubic (FCC) crystal structure at temperatures above 417°C, and a low electron hole number ( $N_r$ ) of 1.66, it transforms to a less ductile hexagonal close packed (HCP) structure at room temperature and has inadequate corrosion resistance to satisfactorily withstand body fluids.

To provide an acceptable level of corrosion resistance, it was necessary to add chromium. However, chromium imparts low stacking fault energy (SFE) and, in fact, raises, rather than lowers, the temperature at which cobalt transforms to a brittle HCP structure. Chromium also has a relatively high electron hole number ( $N_r$ ) of 4.66 and accordingly substantially increases the average electron hole number  $\bar{N}_r$  of the alloy and promotes the formation of brittle phases in the alloy. As a result, a minimum amount of chromium consistent with the required corrosion resistance properties in the alloy should be used.

To counteract the embrittlement imparted by the necessary addition of chromium, nickel, which has an electron hole number ( $N_r$ ) of 0.66 and is very ductile, was added. Nickel also raises the SFE of the alloy to aid in offsetting the adverse effect of chromium on the transformation of cobalt.

The alloy base of cobalt, chromium, and nickel for a dental alloy is a compromise of conflicting mechanical properties of the alloy and physical properties of cobalt, chromium, and nickel. An alloy base having cobalt as the major element, should contain chromium in an amount to provide a minimum of about 20 percent chromium in the final alloy and preferably at least a like amount of nickel. An alloy base of about 35 to 45 percent Co, 20 to 32 percent Cr, and 30 to 40 percent Ni, by weight, and preferably 40 percent Co, 30 percent Cr, and 30 percent Ni provides an excellent balance of mechanical properties, high stacking fault energy, and low average electron hole number, in the alloy base for a dental alloy. Such an alloy base has a yield strength of 44,000 psi, an ultimate tensile strength of 81,000 psi and a ductility as indicated by percent elongation of 31 percent.

As indicated above, this invention contemplates the strengthening of an alloy with minimum adverse effect on its ductility. This is accomplished by selecting strengthening elements for incorporation in the alloy which raise the stacking fault energy (SFE) of the alloy so as to increase the proportion of face centered cubic (FCC) structure in the alloy matrix at room temperature, which will not substantially raise the average electron hole number  $\bar{N}_r$  of the alloy matrix, and which form coherent compounds with cobalt.

Further, the metallic elements selected for strengthening should have sufficient solubility in cobalt to produce a significant effect in raising the SFE of the alloy matrix and to cause the precipitation of coherent intermetallic compounds. However, the solubility of the strengthening element should not be sufficient to cause significant increase in the average electron hole number ( $\bar{N}_r$ ) of the alloy matrix and thereby result in the formation of embrittling phases.

I have found that tantalum and niobium, despite having very large electron hole numbers ( $N_r$ ) of 5.66 which would be expected to promote a high level of formation of brittle phases in the alloy matrix, offer unusual advantages as alloying elements for strengthening a cobalt-base alloy without embrittling the alloy.

The solubility of tantalum and niobium in the cobalt-base alloy is sufficient (4.5 atomic percent) to produce significant solid solution hardening and combine with cobalt to form coherent precipitate particles of  $\text{Co}_3\text{Ta}$  and  $\text{Co}_3\text{Nb}$ .

In addition to the low levels of solubility of Ta and Nb in the alloy matrix, their effective concentration as solute elements in the matrix is further reduced by their precipitation as intermetallic compounds thus contributing no significant effect in raising  $\bar{N}_r$  thereby restricting the formation of embrittling phases.

Further, Ta and Nb significantly increase the stacking fault energy (SFE) of cobalt so that the alloy remains in the ductile face centered cubic (FCC) structure at room temperature rather than the less ductile hexagonal close packed (HCP) structure in which currently available cobalt and cobalt dental alloys normally occur at room temperature. Moreover, the coherent precipitates of tantalum and niobium are fine,

uniformly distributed throughout the alloy, and have close center-to-center distances.

Other elements such as carbon, molybdenum, tungsten, titanium, vanadium, zirconium, boron, silicon, manganese and magnesium, and combinations including such elements, have been used to strengthen cobalt alloys. However, these elements and combinations of elements do not meet the requirements of this invention in one or more respects.

While carbon is a highly efficient strengthener due to the formation of carbides in cobalt-base alloys, and is more effective than tantalum or niobium in increasing the SFE of the alloy, an alloy made accordingly to this invention must be essentially free of carbon. Not only does the presence of carbon in small quantities, e.g., 0.2 percent, result in carbide precipitation strengthening which is highly incoherent, but also the limited amount of carbon which is soluble precludes its use in raising the SFE of the alloy. As a result, a cobalt-base alloy containing sufficient carbon to produce a yield strength of 80,000 psi is brittle with an elongation limited to about 2 to 4 percent. Thus, in the practice of this

cobalt alloys, causes a high proportion of an embrittling phase formation. Accordingly, significant amounts of titanium should be avoided.

Vanadium and Zirconium, among other adverse properties, have very little effect on SFE and high  $N_r$  values of 5.66 to impart, if present in significant amounts, adverse effects on ductility.

The effect of boron as a strengthening element is similar to that of carbon.

Accordingly, as stated above, this invention involves the use of tantalum or niobium as the essential strengthening element for a cobalt base alloy to achieve the objective of providing a superior dental alloy system with maximum ductility, and strength. While the use of molybdenum, titanium and tungsten to partially replace tantalum or niobium is possible with inferior results, the presence of these and other elements and combination of elements as the major strengtheners will have detrimental effects.

Starting with the materials shown in Table I, alloys having the compositions set forth in Table II were made.

Table I

| Chemical Analysis of Elements Percent by Weight |       |       |       |     |       |      |      |      |       |        |
|-------------------------------------------------|-------|-------|-------|-----|-------|------|------|------|-------|--------|
|                                                 | Co    | Ni    | Cr    | Ta  | S     | C    | Fe   | Cu   | Si    | Others |
| Co                                              | 99.91 | 0.061 | —     | —   | .001  | .005 | .007 | .004 | .001  | .00368 |
| Cr                                              | —     | —     | 99.98 | —   | —     | .007 | .003 | —    | —     | .010   |
| Ni                                              | —     | 99.96 | —     | —   | trace | .020 | .003 | .003 | trace | .014   |
| Ta                                              | —     | —     | —     | 100 | —     | —    | —    | —    | —     | —      |

invention, the alloy should be essentially free of carbon and the maximum carbon which can be tolerated is about 0.1 percent.

Molybdenum combines with cobalt and cobalt-base alloys to form a coherent precipitate. However, molybdenum lowers the SFE of the alloy which raises, rather than lowers, the transformation temperature of a cobalt alloy and maintains the presence of the less ductile HCP structure at room temperature. In addition, molybdenum has a high  $N_r$  of 4.66. This high  $N_r$  coupled with a solubility in the cobalt of about four times that of tantalum, results in a high  $N_r$  of the alloy to cause the formation of high percentages of embrittling phases in the alloy. Further, its high solubility eliminates, as a practical matter, the possibility of precipitation strengthening. Moreover, molybdenum reduces the oxidation resistance of the alloy. Accordingly, a cobalt-base alloy is preferably free of molybdenum as an effective strengthening agent and its presence can be tolerated only to the extent that other elements, such as chromium, which have an adverse effect on the SFE and  $N_r$  of the alloy, are reduced to compensate for the presence of the molybdenum. Alternatively, the amount of elements such as nickel, which has a favorable effect on  $N_r$  and SFE can be increased to offset the adverse effects of molybdenum.

Tungsten is similar to molybdenum since it lowers, rather than raises the SFE of the alloy, has a high  $N_r$  value of 4.66 and a solubility in cobalt of about the same level as molybdenum to cause a high  $N_r$  in the alloy matrix.

Titanium has poor body acceptability as well as very poor oxidation resistance during alloying so that it is difficult to alloy and an alloy having a significant amount of titanium cannot be reused through conventional dental procedures. Titanium further has little effect on the SFE of cobalt alloys, has an  $N_r$  higher than molybdenum which, coupled with a high solubility in

Table II

| Composition Percent by Weight   |      |      |      |      |
|---------------------------------|------|------|------|------|
| Alloy                           | Co   | Cr   | Ni   | Ta   |
| A <sub>1</sub> B <sub>1</sub>   | 40   | 30   | 30   | 0    |
| A <sub>2</sub> B <sub>2</sub>   | 39.2 | 29.4 | 29.4 | 2.0  |
| A <sub>3</sub> B <sub>3</sub>   | 38.4 | 28.8 | 28.8 | 3.9  |
| A <sub>4</sub> B <sub>4</sub>   | 38.1 | 28.6 | 28.6 | 4.8  |
| A <sub>5</sub> B <sub>5</sub>   | 37.7 | 28.3 | 28.3 | 5.7  |
| A <sub>6</sub> B <sub>6</sub>   | 37.0 | 27.8 | 27.8 | 7.4  |
| A <sub>7</sub> B <sub>7</sub>   | 36.3 | 27.3 | 27.3 | 9.1  |
| A <sub>8</sub> B <sub>8</sub>   | 35.7 | 26.8 | 26.8 | 10.7 |
| A <sub>9</sub> B <sub>9</sub>   | 35.1 | 26.3 | 26.3 | 12.3 |
| A <sub>10</sub> B <sub>10</sub> | 34.9 | 26.2 | 26.2 | 12.7 |
| A <sub>11</sub> B <sub>11</sub> | 34.8 | 26.1 | 26.1 | 13.0 |
| A <sub>12</sub> B <sub>12</sub> | 34.6 | 26.0 | 26.0 | 13.4 |
| A <sub>13</sub> B <sub>13</sub> | 34.5 | 25.9 | 25.9 | 13.8 |
| A <sub>14</sub> B <sub>14</sub> | 33.9 | 25.4 | 25.4 | 14.2 |
| A <sub>15</sub> B <sub>15</sub> | 33.3 | 25.0 | 25.0 | 16.7 |

The cobalt and nickel were in the form of shot, chromium in 2 × 2 mm sections of crushed sheet, and tantalum in fine wire form cut into lengths 2 to 4 mm.

The alloys were made in zircon-lined crucible and melted in a centrifugal-induction furnace containing a vacuum system. The lower melting elements cobalt and nickel were placed on top of the chromium. During melting, the cobalt and nickel melted earlier than chromium, flowed to coat it and minimized the oxidation of chromium as it melted.

Standardized test specimens for tensile testing were prepared in accordance with American Dental Association Specification Number 14 to establish suitability of the alloys for dental applications.

Ultimate tensile strength, 0.2 percent offset yield strength, percent elongation, and hardness were determined.

The data obtained from testing the several samples of each alloy composition for elongation, 0.2 percent offset yield strength, ultimate tensile strength and hardness are given in Tables III, IV, V, and VI.

The mean elongation values of the prepared alloys

together with the values in the 95 percent confidence limits are given in Table III.

Table III

| Alloy                           | % Elongation<br>(Mean) | Elongation, % |               | 95% Confidence<br>Limits |
|---------------------------------|------------------------|---------------|---------------|--------------------------|
|                                 |                        | Std.<br>Dev.  | Std.<br>Error |                          |
| A <sub>1</sub> B <sub>1</sub>   | 30.9                   | 0.9           | 0.45          | 29.5-32.3                |
| A <sub>2</sub> B <sub>2</sub>   | 30.6                   | 1.4           | 0.70          | 28.4-32.8                |
| A <sub>3</sub> B <sub>3</sub>   | 27.7                   | 2.6           | 1.30          | 23.5-31.8                |
| A <sub>4</sub> B <sub>4</sub>   | 28.4                   | 1.2           | 0.60          | 26.5-30.3                |
| A <sub>5</sub> B <sub>5</sub>   | 28.0                   | 2.1           | 1.0           | 24.5-31.5                |
| A <sub>6</sub> B <sub>6</sub>   | 26.5                   | 1.9           | 0.95          | 23.5-29.5                |
| A <sub>7</sub> B <sub>7</sub>   | 20.1                   | 1.4           | 0.70          | 17.9-22.3                |
| A <sub>8</sub> B <sub>8</sub>   | 21.3                   | 2.1           | 1.1           | 17.8-24.8                |
| A <sub>9</sub> B <sub>9</sub>   | 18.0                   | 2.7           | 1.35          | 13.7-22.3                |
| A <sub>10</sub> B <sub>10</sub> | 13.3                   | 0.8           | 0.40          | 12-14.6                  |
| A <sub>11</sub> B <sub>11</sub> | 9.9                    | 1.3           | 0.65          | 7.8-12.0                 |
| A <sub>12</sub> B <sub>12</sub> | 6.4                    | 0.5           | 0.25          | 5.6-7.2                  |
| A <sub>13</sub> B <sub>13</sub> | 5.5                    | 0.9           | 0.45          | 4.1-6.9                  |
| A <sub>14</sub> B <sub>14</sub> | 4.6                    | 0.7           | 0.35          | 3.5-5.7                  |
| A <sub>15</sub> B <sub>15</sub> | 4.7                    | 0.9           | 0.45          | 3.3-6.1                  |

The elongation, decreased with tantalum concentration from 30.9 percent for the alloy-base A<sub>1</sub>B<sub>1</sub> containing no tantalum, to 4.7 percent for alloy A<sub>15</sub>B<sub>15</sub> containing 16.7 percent tantalum. When the tantalum concentration was increased in increments of 2 gms per 100 gms of the alloy-base, the elongation decreased gradually. For example, when tantalum concentration was increased from 10.7 percent in alloy A<sub>9</sub>B<sub>9</sub> to 12.3 percent in alloy A<sub>9</sub>B<sub>9</sub>, the elongation was decreased from 21.3 to 18.0 percent. This gradual and slow response of ductility to tantalum addition was true for alloys A<sub>1</sub>B<sub>1</sub> to A<sub>9</sub>B<sub>9</sub>. However, when the tantalum concentration was increased from 12.3 percent in alloy A<sub>9</sub>B<sub>9</sub> to 13.8 percent in alloy A<sub>13</sub>B<sub>13</sub>, there was an accelerated decrease in ductility with elongation decrease from 18.0 to 5.5 percent. The sudden reduction in ductility of alloys A<sub>10</sub>B<sub>10</sub> to A<sub>12</sub>B<sub>12</sub> indicate a critical maximum limit of tantalum in the range of 12.3 to 13.8 percent indicative of the fact that beyond this concentration, further addition of tantalum contributed significantly to raising N<sub>e</sub>, thus causing the formation of embrittling phases.

The mean values of the 0.2 percent offset yield strength of the prepared alloys, together with the values for 95 percent confidence limits are given in Table IV.

Table IV

| Alloy                           | Mean    | 0.2% Yield Strength, psi |               | 95% Confidence<br>Limits |
|---------------------------------|---------|--------------------------|---------------|--------------------------|
|                                 |         | Std.<br>Dev.             | Std.<br>Error |                          |
| A <sub>1</sub> B <sub>1</sub>   | 44,000  | 1,865                    | 930           | 41,000-47,000            |
| A <sub>2</sub> B <sub>2</sub>   | 48,300  | 3,500                    | 1,750         | 42,800-53,900            |
| A <sub>3</sub> B <sub>3</sub>   | 55,000  | 2,880                    | 1,440         | 50,400-59,600            |
| A <sub>4</sub> B <sub>4</sub>   | 56,300  | 714                      | 360           | 55,200-57,400            |
| A <sub>5</sub> B <sub>5</sub>   | 60,400  | 3,200                    | 1,600         | 55,300-65,500            |
| A <sub>6</sub> B <sub>6</sub>   | 59,300  | 334                      | 170           | 58,800-59,800            |
| A <sub>7</sub> B <sub>7</sub>   | 70,400  | 665                      | 330           | 69,400-71,500            |
| A <sub>8</sub> B <sub>8</sub>   | 73,700  | 3,800                    | 1,900         | 67,700-79,700            |
| A <sub>9</sub> B <sub>9</sub>   | 80,400  | 2,657                    | 1,330         | 76,200-84,600            |
| A <sub>10</sub> B <sub>10</sub> | 82,400  | 1,650                    | 830           | 79,800-85,000            |
| A <sub>11</sub> B <sub>11</sub> | 90,600  | 5,700                    | 2,850         | 81,500-99,700            |
| A <sub>12</sub> B <sub>12</sub> | 96,700  | 1,050                    | 530           | 95,000-98,400            |
| A <sub>13</sub> B <sub>13</sub> | 98,800  | 5,100                    | 2,550         | 90,700-107,000           |
| A <sub>14</sub> B <sub>14</sub> | 99,900  | 4,210                    | 2,100         | 93,200-106,600           |
| A <sub>15</sub> B <sub>15</sub> | 108,200 | 10,240                   | 5,120         | 91,300-125,100           |

The yield strength increased with tantalum concentration from  $44 \times 10^3$  psi for the tantalum-free alloy

A<sub>1</sub>B<sub>1</sub> to  $108 \times 10^3$  psi for alloy A<sub>15</sub>B<sub>15</sub> containing 16.7 percent tantalum. As in the case of elongation, the value of the yield strength increased rapidly in the tantalum range 12.3 to 13.8 percent represented by alloys A<sub>9</sub>B<sub>9</sub> to A<sub>13</sub>B<sub>13</sub>. The yield strength increased from  $80.4 \times 10^3$  psi for the former alloy to  $98.8 \times 10^3$  psi for the latter. At tantalum concentrations of less than 12.3 percent, the increase in the yield strength was essentially gradual.

The accelerated response of both properties to tantalum addition occurred in the same region. Further, the response of the elongation (reduction by %) was significantly more rapid than that of the yield strength (increase by ¼), indicating that embrittling phase formation was accelerated.

It should be noted from tables III and IV that the addition of up to 6 percent tantalum caused significant increase in yield strength (44,000 to 60,000 psi) and insignificant reduction in ductility (31 to 28 percent elongation). This favorable result is due to the excellent effect of tantalum in raising the SFE of the alloy thereby increasing the concentration of the ductile FCC in alloy and at the same time strengthened the alloy by its effect as a solid solution hardener. Thus, the addition of tantalum in these percentages surprisingly increased the strength substantially with insignificant reduction of ductility.

The results of testing for the ultimate tensile strength were treated in a similar fashion to those of the yield strength and are given in Table V as follows:

Table V

| Alloy                           | Mean    | Ultimate Tensile Strength, psi |               | 95% Confidence<br>Limits |
|---------------------------------|---------|--------------------------------|---------------|--------------------------|
|                                 |         | Std.<br>Dev.                   | Std.<br>Error |                          |
| A <sub>1</sub> B <sub>1</sub>   | 80,300  | 1,800                          | 900           | 77,400-83,200            |
| A <sub>2</sub> B <sub>2</sub>   | 78,000  | 3,500                          | 1,750         | 72,400-83,600            |
| A <sub>3</sub> B <sub>3</sub>   | 82,600  | 900                            | 450           | 81,200-84,000            |
| A <sub>4</sub> B <sub>4</sub>   | 84,000  | 1,000                          | 500           | 82,400-85,600            |
| A <sub>5</sub> B <sub>5</sub>   | 102,100 | 4,900                          | 2,450         | 94,300-109,900           |
| A <sub>6</sub> B <sub>6</sub>   | 101,100 | 1,700                          | 850           | 98,400-103,800           |
| A <sub>7</sub> B <sub>7</sub>   | 105,800 | 7,000                          | 3,500         | 94,700-116,900           |
| A <sub>8</sub> B <sub>8</sub>   | 106,500 | 3,300                          | 1,650         | 101,300-111,800          |
| A <sub>9</sub> B <sub>9</sub>   | 121,300 | 2,660                          | 1,330         | 117,100-125,500          |
| A <sub>10</sub> B <sub>10</sub> | 122,300 | 1,650                          | 1,330         | 118,100-126,500          |
| A <sub>11</sub> B <sub>11</sub> | 124,500 | 1,100                          | 550           | 122,800-126,300          |
| A <sub>12</sub> B <sub>12</sub> | 127,000 | 8,000                          | 4,000         | 114,300-139,700          |
| A <sub>13</sub> B <sub>13</sub> | 125,500 | 8,300                          | 4,150         | 112,300-138,700          |
| A <sub>14</sub> B <sub>14</sub> | 136,000 | 8,900                          | 4,450         | 121,800-150,200          |
| A <sub>15</sub> B <sub>15</sub> | 133,300 | 8,300                          | 4,150         | 120,100-146,500          |

The ultimate tensile strength increased from  $80.3 \times 10^3$  psi as the tantalum concentration was changed from zero (A<sub>1</sub>B<sub>1</sub>) to 16.7 (A<sub>15</sub>B<sub>15</sub>) percent. Just as in the cases of the yield strength and elongation, the U.T.S. had a sudden change as the tantalum concentration was varied from 10.7 to 12.3 percent.

The hardness of selected alloy compositions is given in Table VI is easily within the range of current commercial dental alloys.

Table VI

| Alloy                         | Hardness                 |  |
|-------------------------------|--------------------------|--|
|                               | Knoop Hardness No. (KHN) |  |
| A <sub>1</sub> B <sub>1</sub> | 232                      |  |
| A <sub>3</sub> B <sub>3</sub> | 285                      |  |
| A <sub>6</sub> B <sub>6</sub> | 310                      |  |

Table VI-Continued

| Alloy                           | Hardness                 |
|---------------------------------|--------------------------|
|                                 | Knoop Hardness No. (KHN) |
| A <sub>8</sub> B <sub>8</sub>   | 321                      |
| A <sub>11</sub> B <sub>11</sub> | 328                      |
| A <sub>13</sub> B <sub>13</sub> | 350                      |
| A <sub>14</sub> B <sub>14</sub> | 353                      |
| A <sub>15</sub> B <sub>15</sub> | 355                      |

Niobium may be substituted for tantalum in the ratio of about 60 percent niobium to 100 percent tantalum, by weight. About 12.7 percent is the maximum amount of tantalum (about 7 percent niobium) which can be added to the preferred base alloy without exceeding its critical average electron hole number ( $\bar{N}_r$ ). The addition of any excess tantalum (or niobium) will result in substantial increase of  $\bar{N}_r$  of the alloy and decrease its ductility by the formation of embrittling phases. However, tantalum may be present in amounts of up to about 17 percent (niobium about 10 percent) and the alloy will still have mechanical properties equal to or exceeding those of the presently available commercial dental alloys as indicated in Tables III through VI for composition A<sub>15</sub>B<sub>15</sub>.

Moreover, an increase of nickel in the alloy base of about 10 percent by weight, will increase the requirements of tantalum approximately 1 percent, by weight, to obtain essentially the same mechanical properties of the alloy, and a decrease of chromium in the alloy base of 10 percent, by weight will increase the percentage requirements of tantalum in the alloy by approximately 3 percent, by weight, to obtain essentially the same mechanical properties of the alloy. Thus an alloy base consisting of 40 parts cobalt, 20 parts chromium, and 40 parts nickel, by weight will have similar mechanical properties to the A<sub>10</sub>B<sub>10</sub> alloy if it contains 14.5 percent tantalum by weight, and the same alloy base with about 21 percent tantalum will have similar mechanical properties to the A<sub>15</sub>B<sub>15</sub> alloy. Such adjustments in nickel, chromium and tantalum content will produce an average electron hole number ( $\bar{N}_r$ ) of the alloy which is essentially the same as corresponding alloys indicated.

Platinum, palladium, and iron can be substituted for nickel in the alloy. Platinum and palladium are expensive, however, and iron has an electron hole number ( $N_r$ ) of 2.66 which is substantially higher than that of nickel. Accordingly, where iron is substituted for nickel in the alloy, in whole or in part, there should be a compensating reduction in the elements of relatively high  $N_r$  in the alloy to produce the same average electron hole number ( $\bar{N}_r$ ) as the corresponding alloy containing nickel instead of iron.

From the foregoing, it is readily apparent that the cobalt-base dental alloy system of this invention provide the mechanical properties desired for different dental applications through the utilization of tantalum or niobium as the essential strengthening agent.

As will be apparent to persons skilled in the art, various modifications of the above described invention will become readily apparent with departure from the spirit and scope of the invention.

I claim:

1. A cobalt-base dental alloy essentially free of carbon and having an alloy base comprising cobalt in an amount, by weight, of about 35 to 45 percent, chromium in an amount, by weight, of about 20 to 32 percent, and nickel in an amount, by weight, of about 30 to 40 percent as essential major alloying elements, and a member of the group comprising tantalum and niobium alloyed therewith as the major strengthening element, said strengthening element being present in an amount sufficient to form coherent intermetallic precipitates with cobalt.

2. The alloy of claim 1 wherein iron is substituted in whole or in part for nickel.

3. The alloy of claim 1 wherein tantalum is present in the alloy in an amount of 7.5 to 17 percent, by weight.

4. The alloy of claim 1 wherein tantalum is present in an amount of about 12 to 17 percent, by weight.

5. The alloy of claim 1 wherein niobium is present in an amount of about 6 to 9 percent, by weight.

6. A denture casting made of the alloy of claim 1.

\* \* \* \* \*