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## Abstract

Today Vitallium is used for surgical implants. It is a casting alloy which, with advances in casting technology, is also used commercially for making instruments of fairly complex shape. Because of its expense, however, it is not widely used in Japan. Instead, a series of 18-8 Mo alloys are used in Japan even though of insufficient strength. Used over a long period of time in the body, especially for the purpose of preserving structual functions as part of the human skeleton, it often corrodes, resulting in either abnormalities in tissue cells or, because of its insufficient strength, danger of bending and breaking with aging. In spite of a marked advance in fracture treatment, we have hardly any suitable materials for making instruments appropriate to the internal fixation of fractures in Japan. We, therefore, conducted various experiments to develop an alloy with sufficient corrosive resistance and strength that could be formed into a complex shape to take the place of Vitallium alloy, finally succeeding in developing an alloy we call "COP". The characteristic properties of COP may be summarized as follows: 1. The main components are 20% Cr, 20% Ni, 20% Co and 4% Mo aside from 0.2% P. 2. As it contains "P", it shows a marked age-hardening. In its molten state its machinability is excellent, and later it can readily be hardened by heat-treatment. 3. It has not only a marked yield point and tensile strength but also has toughness in elongation and reduction of area, showing a strength which surpasses Vitallium. 4. Its corrosive resistance is great. 5. Its cost is far cheaper than Vitallium.

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# COP, A NEW ALLOY FOR SURGICAL IMPLANTS

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*Abstracts.* Today Vitallium is used for surgical implants. It is a casting alloy which, with advances in casting technology, is also used commercially for making instruments of fairly complex shape. Because of its expense, however, it is not widely used in Japan. Instead, a series of 18-8 Mo alloys are used in Japan even though of insufficient strength. Used over a long period of time in the body, especially for the purpose of preserving structual functions as part of the human skeleton, it often corrodes, resulting in either abnormalities in tissue cells or, because of its insufficient strength, danger of bending and breaking with aging. In spite of a marked advance in fracture treatment, we have hardly any suitable materials for making instruments appropriate to the internal fixation of fractures in Japan. We, therefore, conducted various experiments to develop an alloy with sufficient corrosive resistance and strength that could be formed into a complex shape to take the place of Vitallium alloy, finally succeeding in developing an alloy we call "COP". The characteristic properties of COP may be summarized as follows: 1. The main components are 20% Cr, 20% Ni, 20% Co and 4% Mo aside from 0.2% P. 2. As it contains "P", it shows a marked age-hardening. In its molten state its machinability is excellent, and later it can readily be hardened by heat-treatment. 3. It has not only a marked yield point and tensile strength but also has toughness in elongation and reduction of area, showing a strength which surpasses Vitallium. 4. Its corrosive resistance is great. 5. Its cost is far cheaper than Vitallium.

Many types of alloys are being used for the internal fixation of fractures, but 18–8 Mo stainless steel and Vitallium are the principal materials in use today. Prior to World War II, 18–8 stainless steel was the main material in the USA, but owing to its many shortcomings as a surgical implant, an alloy belonging to the 18–8 Mo series has taken its place (1. 2).

Vitallium, first developed for the dental field by Austenal Laboratories in 1929, has been used extensively in bone and joint surgery for surgical implants, mainly in the USA. It was also used during World War II in turbines and rocket engines as a heat resistant alloy because of its superior resistance to creep and stress ruptures of modified Co-Cr-Mo alloy (1, 3). It is impossible to harden 18–8 Mo stainless steel by heat treatment as it requires cold working for hardening.

Cold working has many disadvantages since cutting work is difficult or cannot be done at more than $H_RC$ 30 in hardness, so it is usually performed at $H_RC$ 15-20 in Japan, consequently it is apt to bend and break during use (4-7).

Vitallium is also an excellent alloy material. Its main components are 0.28% C, 28% Cr, 6% Mo and 62% Co. Since hot working is not possible with it, it cannot be used in making the matrix of instruments because of its hardness in cutting work. Therefore, in making an instrument with this alloy, precision casting has to be resorted to, making its cost prohibitivly high. To overcome these difficulties we have developed a strong alloy material, "COP" (one of the PH stainless steel), which can be hardened by heat treatment (also cold working) and has strong corrosive resistance and machinability such that it can readily be molded in the matrix of the apparatus for the internal fixation of the fractures (4, 7, 8).

The alloy is manufactured by Tokushu-Seiko Co. and the instrument by Mizuho Medical Instruments Industries Ltd. Adaptability tests were conducted by the staff of the Department of Orthopedic Surgery, Okayama University Medical School. Surgical implant tests were conducted in the Laboratories of the Engineering School, Department of Technology, OkayamaUniversity.

## PROPERTIES OF COP

*Features of COP*

In order to secure properties equal to those of the Vitallium alloy, COP was made to contain 0.2% P, 0.2% C, 20% Cr, 20% Ni, 20% Co and 4% Mo (Table 1), so that by the solution treatment, it can be softened to 10 $H_RC$ in hardness, giving sufficient machinability. Moreover, by tempering at 780°C it can be hardened to over 30 $H_RC$ by precipitation hardening, resulting in a tensile strength of over 100kg/mm², with toughness in elongation and reduction of area as well as a corrosive resistance superior to Vitallium alloy. The difference from Vitallium is that COP can be shaped into any complex form because of its machinability and that it can be readily hardened by simple heat treatment to a hardness equal to Vitallium (4, 6, 7).

TABLE 1. CHEMICAL COMPOSITION OF EXAMINED METALS

| Alloys | C | Si | Mn | P | S | Ni | Cr | Mo | Co |
|---|---|---|---|---|---|---|---|---|---|
| SMo (AISI 316L) | 0.03 | 1.00 | 2.00 | 0.040 | 0.030 | 12.00～16.00 | 16.00～18.00 | 2.00～3.00 | |
| AOI | 0.08 | 0.39 | 1.77 | 0.018 | | 12.27 | 17.72 | 2.73 | |
| Vitallium | 0.23 | 0.68 | 0.94 | 0.013 | 0.009 | | 27.80 | 5.93 | 64.30 |
| COP | 0.27 | 0.54 | 1.22 | 0.145 | 0.010 | 19.95 | 20.54 | 3.81 | 20.48 |

*Heat treatment and hardness*

1. *Solution treatment conditions*. When COP was kept at 1,000-1,200°C for one hour after heat treatment and then given solution treatment, it softened as

shown in Fig. 1, *i.e.* at 1,150°C to 12-13.5 $H_RC$. In contrast, Vitallium at 1,150°C was about 35 $H_RC$ and did not soften even after solution treatment. At 1,200°C it remained at 31.5 $H_RC$. S-816 in the forging state was 34 $H_RC$, and at 1.180°C it softened to 24 $H_RC$ by solution treatment. Compared with COP, both of them were considerably harder.

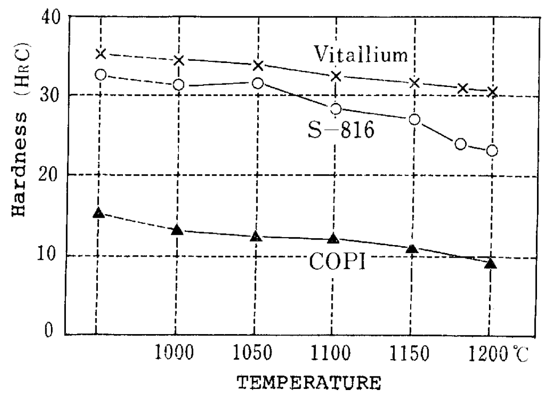


Fig. 1. Solution treatment of various alloys. Solution treatment of alloys were conducted after heat treatment at the indicated temperature for 1 hr. Hardness is shown in the unit of Rockwell hardness.

2. *Hardness at aging.* COP was subjected to one hour heat treatment at 1,150°C and tempered at 750°C, 780°C and 810°C respectively for 0.5-50 hours, then hardened by aging as illustrated in Fig. 2. Namely, aging for 30 minutes

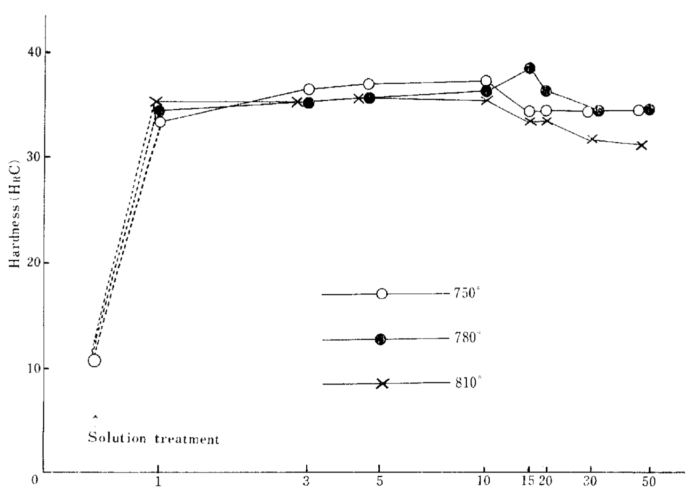


Fig. 2. Effect of aging on hardness of COP. COP treated at 1.150°C and tempered at 750°C, 780°C, and 810°C, and then heated by aging. ($H_RC$=Hardness at Rockwell C scale)

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produced a considerable rise in hardness and after one hour, sufficient hardening of over 30 $H_RC$ could be attained.

3. *Mechanical properties.* The mechanical properties of Vitallium and COP in the state of solution treatment as well as in aging are shown in Table 2. Cast Vitallium shows tensile strength of 75 kg/mm², 4-8% elongation and 32 $H_RC$ at hardness, but in wrought Vitallium in both the solution treatment state and aging after solution treatment, the tensile strength was 107-108 kg/mm², 21% elongation and 34-35 $H_RC$, showing fairly good toughness. In contrast, COP in the solution treatment state had a tensile strength of 81 kg/mm², 51% elongation, about 56% in the reduction of area and was sufficiently soft at 10 $H_RC$, indicating good machinability. When the materials were aged at 780°C for 6 hours, the tensile strength became 106 kg/mm², 22-24% elongation, 24-34% in the reduction of area, and 33-36 $H_RC$, showing a strength practically identical with Vitallium but a toughness which was rather higher.

TABLE 2. EXAMINATION OF TENSILE STRENGTH AT ROOM TEMPERATURE

| Alloys | Treatment | Yielding point (kg/mm²) | Tensile strength (kg/mm²) | Elongation (%) | Hardness ($H_RC$) |
|---|---|---|---|---|---|
| COP | Solution treatment | | 8.16 | 51.0 | 11 |
| | Thermal aging | 67.7 | 106.5 | 24.1 | 33 |
| Vitallium | Solution treatment | 75.5 | 108.6 | 21.3 | 35 |
| | Thermal aging | 69.7 | 107.6 | 21.2 | 34 |

*Corrosive resistance*

1. *Immersion test.* For the immersion test the solutions listed in Table 3 were used. The samples of alloys tested were COP, Vitallium and 18-8 Mo, each cut into a piece of about 10 mm³ in dimension, and immersed in each solution at 37°C for 72 consecutive hours. None of the materials showed any abnormlities such as discoloration, pitting, etc. and the loss by corrosion proved to be minimal.

TABLE 3. CORROSIVE SOLUTIONS USED FOR IMMERSION TEST

| | |
|---|---|
| 0.05% HCl | 10% $HNO_3$ |
| 1.0% NaCl | 10% HCl |
| 0.05% $HNO_3$ | 10% $H_2SO_4$ |
| 1.0% lactic acid | 10% NaCl |
| 1.0% Sod. sulfate | 10% NaOH |
| Mixed solutions | |
| Glucose | 10% |
| Lactic acid | 10% |
| Acetic acid | 2% |
| Ammonium sulfate | 2% |

2. *Corrosion in boiling acids.* Corrosion tests in boiling acids were conducted with 40% nitric acid and acetic acid. The results were about the same for each alloy as shown in Table 4.

TABLE 4. LOSS BY CORROSION IN BOILING ACIDS

| Alloys | 40% $HNO_3$ | | 10% acetic acid | |
|---|---|---|---|---|
| | Solution treatment | Aging | Solution treatment | Aging |
| COP | <0.10 | <0.18 | <0.08 | <0.10 |
| Vitallium | <0.11 | <0.15 | <0.05 | <0.05 |
| 18-8 Mo | <0.10 | <0.10 | <0.10 | <0.10 |

* Examined alloys show only slight loss by corrosion in boiling acids.

3. *Stress corrosion.* The stress corrosion test was carried out with test pieces of beam type. The test piece was 3 mm in thickness, and stress was given to it by pressing the bolt so as to produce a deflection of 0.8 mm. Each piece was then immersed in various solution and kept at 37°C for 72 hours. No abnormality was seen after this immersion (Table 5). Since alloy of high tensile strength cracks within a relatively short time after immersion in a boiling solution of 42% magnesium chloride, the same immersion tests in boiling solutions were conducted. As a result it was demonstrated that COP and Vitallium immersed over 92 hours did not show any cracks, but that 18-8 Mo and 18 Mn-3 Cr stainless steel had cracks within 3 to 6 hours as illustrated in Table 5. Neither COP nor Vitallium crack, therefore, even in the state of high hardness.

TABLE 5. CRACKING TIME IN BOILING SOLUTION

| Alloys | Solution treatment | | | Aging | | |
|---|---|---|---|---|---|---|
| | Hardness | 0.8 mm (hr) | 2.0 mm (hr) | Hardness | 0.8 mm (hr) | 2.0 mm (hr) |
| COP | $H_RC$ 11 | >77 | >33 | $H_RC$ 34 | >92 | >46 |
| Vitallium | $H_RC$ 34 | >77 | >33 | $H_RC$ 33 | >92 | >46 |
| 18-8 Mo | $H_RB$ 88 | >77 | >33 | $H_RC$ 34.5 | 6.5 | 2.66 |
| 18-8 Mn-3 Cr | | | | $H_RC$ 34.5 | 3.6 | 2.16 |

* COP (hardened by aging) and Vitallium show resistant to crack in boiling solution.

## TECHNOLOGICAL STUDY OF TRIAL SURGICAL IMPLANTS OF COP

The surgical implants so far made with COP include Jewett nail-plates, clover-leaf nails, AO type plates and screws, AO type angle plates and femoral condyle prostheses. For the prosthesis, we make it a rule to mold the original shape by precision casting of Lost-Wax method to take advantage of COP's special properties and finish it to the necessary hardness by heat treatment. We also made a comparative study of trial AO type plates and screws and cloverleaf nails made of 18-8 Mo and Vitallium.

*Discussion of metals used as the material*

In our chemical analysis of the components contained in the plates and screws available in Japan and foreign countries, we found that the majority were made with 18–8 Mo stainless steel (SUS 32, AISI 316 or 316 or 316L) composed of 18% Cr, 8% Ni and 2.5% Mo as the main components, while some imported ones were made with a cobalt base alloy containing Cr-Mo. There were also a few made with 22A steel and titanium.

AOI products that have come to be used extensively in Japan are made with 18–8 Mo stainless steel. The surface hardness is over 30 $H_RC$ and markedly hard, corresponding to the hardness of Vitallium. This is due to cold working. A look at the distribution of hardness in the cross-section showed that its hardness decreased from surface to center, and microscopic metal tissue showed sliding crystals, a clear indication that it had been strongly hardened by cold working (Fig. 3).

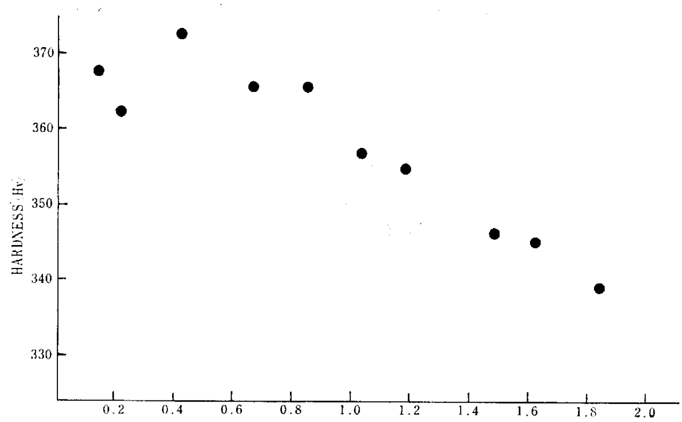


Fig. 3. Distribution of hardness in section of AO plate. In section of AO plate, hardness of surface is strongly high, but in the mid-portion not so. (Hv= Vickers hardness)

It is known that when subjected to cold working, shortcomings such as chemical corrosion, stress corrosion and weakness to heat because of lattice defect occur.

The intramedullary nail labeled as "Vitallium", a product of Howmedica Co. does not show the composition of Vitallium but is a 22 Cr-10 Ni-15 W-Co base alloy, and this is what is known as L-605 (or Stellite 25, Neutrillium or Wrought Vitallium) (7). Vitallium, being a casting alloy, is unsuitable to cutting work, so making a intramedullary nail with it is very difficult. L-605 alloy is therefore used its place. The latter alloy can be hardened to about 50 $H_RC$ by cold working so it is possible to shape it into a nail, but because of its disadvantages it still needs some consideration.

*Strength.*

1. *Plate.* A three-point load deflection test of plate was conducted with an interspace distance of 5 cm. Plates were classified into the following 5 types according to the size and shape of the screw holes:

Type I: Venable type, Type II: slotted plate, Type III: Eggers type, Type IV-A: AO type, narrow plate, Type IV-B: AO type broad plate (Table 6).

TABLE 6. 3-POINT DEFLECTION TEST OF VARIOUS PLATES

| Type | Plates | Material | Hardness | Maximum load | Residual deflection(P) | P/A |
|---|---|---|---|---|---|---|
| Type I | Zimmer | 18-8 Mo | $H_RC$ 24 | 293kg | 182kg | 5.1 |
| | Howmedica | Vitallium | 30 | 125 | 99 | 2.7 |
| Type II | Kodama (M. Co.) | 18-8 Mo | 17 | 175 | 123 | 3.9 |
| | Amako (M. Co.) | 18-8 Mo | 25 | 140 | 122 | 4.6 |
| | Howmedica | Vitallium | 33 | 95 | 65 | 5.8 |
| Type III | Domestic (M.Co.) | 18-8 Mo | 28 | 120 | 120 | 5.0 |
| | Howmedica | Vitallium | 30 | 200 | 155 | 3.4 |
| Type IV-A | AOI | 18-8 Mo | 35 | 250 | 227 | 4.2 |
| | Howmedica | Vitallium | 31 | 297 | 233 | 3.8 |
| | COP | COP | 30 | 215 | 174 | 3.6 |
| Type IV-B | AOI | 18-8 Mo | 33 | 638 | 575 | 11.1 |
| | Howmedica | Vitallium | 29 | 492 | 392 | 5.1 |
| | COP | COP | 34 | 860 | 750 | 10.1 |

When the load was placed in the middle equidistant from the holes ignoring the shape of the plate, it was found that Type IV-B, AO broad plate, was the strongest. An analysis of the maximum load and the load that induces a residual deflection of 1 mm showed that the Vitallium group was not as strong as is generally thought, instead its strength did not differ much from that of 18–8 Mo alloys. Type IV-B was the strongest of the COP groups of Plates. This also applied to the ratio of the load that produced a residual deflection of 1 mm to the area of the cross-section at the loading point (P/A).

2. *Screws.* The screws generally used were divided into two groups of standard type and AO cortical bone type, and drawing tests were conducted with these screws (Table 7). It was demonstrated that the crack-producing load was greater as the minor diameter of the screws was greater. In the case of the Vitallium group both standard type and the AO cortical bone type could not be said to be stronger than 18–8 Mo alloy groups in over-all strength. In comparing

the tensile strength(kg/mm$^2$) with the dividend of the crack-producing load divided by the area of the cross-sectional area calculated from the minor diameter of the screw for convenience, both groups of Vitallium gave unexpectedly small values.

3. *Intramedullary nails.* The over-all strengths of 4 types, domestic 18-8 Mo product, Pohl Co. Product, Howmedica Co. product and COP nail, were tested. It was found that the cross-sectional distribution of hardness varied considerably in all three types of nail other than the COP nail. This variation in hardness seemed to be due to the cold working.

When the deflection tests are conducted as the plates, it was found that Howmedica Co. nail (named "Vitallium", but truly not Vitallium) showed the greatest maximum load (Table 8), and this also was due to cold working. This alone cannot be taken as the best nail. In addition, by cutting the 12mm/intramedullary nail to 2 cm in length, the repulsive force, or the spring constant, was

TABLE 7. TENSILE STRENGTH OF VARIOUS SCREWS

| Type | Alloys | Hardness | Crack-producing load | Tensile strength |
|---|---|---|---|---|
| Standard type | 18-8 Mo | $H_RC$ 31 | 550 kg | 103.7kg/mm |
| | Vitallium | 41 | 590 | 95.9 |
| | COP | 33 | 620 | 116.8 |
| AO-type | AOI | 33 | 790 | 111.8 |
| | Vitallium | 33 | 662 | 87.7 |
| | COP | 34 | 950 | 124.5 |

TABLE 8. 3-POINT DEFLECTION TEST OF VARIOUS NAILS

| Load | Nails | Domestic (M. Co.) | Pohl | Howmedica | COP |
|---|---|---|---|---|---|
| | Materials | 18-8 Mo | 18-8 Mo | Vitallium | COP |
| 50 kg | Observed deflection | 0.59 | 0.115 | 0.068 | 0.080 |
| | Residual deflection | 0 | 0.015 | 0 | 0 |
| 100 kg | Observed deflection | 0.90 | 0.230 | 0.130 | 0.140 |
| | Residual deflection | 0.2 | 0.035 | 0.018 | 0.005 |
| 500 kg | Observed deflection | 2.6 | 0.92 | 0.60 | 0.72 |
| | Residual deflection | 1.35 | 0.42 | 0.15 | 0.21 |
| Maximum load(kg) | | 530 | 750 | 1,505 | 820 |
| Spring constant | tan $\theta$ (kg/mm) | 142 | 152 | 166 | 194 |
| | Elastic limit (kg) | 95 | 120 | 135 | 122 |

measured. The COP nail showed the greatest value of tan $\theta$.

### BIOLOGICAI REACTION

*This test was conducted with rabbits.* With 18–8 Mo, Vitallium alloy and COP as the materials, small plates were made and embedded in subcutaneous and dorsal muscle of rabbits. Tissue reactions with the lapse of time were examined. Kirschner's wire 2 mm in diameter was also inserted intramedullaryly into the rabbit femur and similar examinations were carried out. Furthermore, small sections of 18–8 Mo and COP wires 1 mm in length were made, embedded in the rabbit knee joint, and similarly examined. We found no abnormality in the tissues in any case.

*Tissue cultures.* In this test we used discs 3.5mm in diameter, 1 mm in thickness that were made with 18–8 Mo, Vitallium and COP. The cells used for culture were ME line in culture passage of the 86th generation. These test discs were previously washed well by supersonication, placed in flasks and TD 15 culture bottles, then ME cells were placed in each vessel, and cultured separately with the three kinds of alloys. The results showed no abnormality of the culture cells.

*Clinical application.* We are at present using AO type plates and screws, Jewett nail-plates, Küntscher's intramedullary nails and Kodama-Yamamoto's total knee prostheses on about 500 patients and we find the union of bone progressing smoothly in all fractured cases without any abnormal reactions. X-ray examination of our cases so far reveals no abnormalities such as abnormal callus formation or bone absorption around the COP material (8, 9).

### IMPORTANT POINT IN MANUFACTURING

COP is an alloy on which cutting can readily be done when it is softened to 10 $H_RC$ at hardness after solution treatment, and it can be hardened by aging at high temperature up to over 30 $H_RC$. Therefore, heat treatment is one of the important steps in its preparation and the temperature has to be controlled precisely.

### CONCLUSION

As is obvious from the foregoing investigation, 18–8 Mo alloy is soft and requires cold working to raise its strength. Once subjected to cold working, it is so hard that cutting work becomes quite difficult, hence its finished product, like AOI, becomes very expensive. In addition, there is the danger of various disadvantages due to lattice defects. In the case of Vitallium, it seems that its strength is unquestioned, but its toughness is unexpectedly low and its finishing has to rely on precision casting making its machinability difficult and its cost prohibitively high. We are of the opinion that trial plates, screws and intramedullary nails made with COP are excellent and can be extensively used as attested to by our clinical and experimental results in comparison with other conventional surgical implants available on the market (Table 9).

Table 9. Advantages and disadvantages of examined alloys

| Alloys | Biological stability | Hardness | Method of manufacturing |
|---|---|---|---|
| SMo | Good | $H_RC$ 15 | Easy |
| AOI | Good | 35 | Manufactured after hardening by cold working |
| Vitallium | Excellent | 35 | Casting |
| COP | Good | 33 | Hardened after hot treatment of the manufactured |

We have found that COP *in vivo* does not induce any abnormal reactions and so can safely be used extensively as a material suitable to surgery of bone and joints.

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