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[54] **NIOBIUM-BASED OXIDATION RESISTANT MATERIALS AND PROCESS FOR THEIR PREPARATION**

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[51] **Int. Cl.** **C23f 7/02**

[58] **Field of Search**...................... 117/131, 22, 127, 117/135.1; 148/6.3

[56] **References Cited**

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[57] **ABSTRACT**

Niobium and niobium-based alloys are protected against oxidation by providing them with a protective coating of mixed metallic oxides of the β—Nb_2O_5 type.

6 Claims, 5 Drawing Figures

Fig. 1

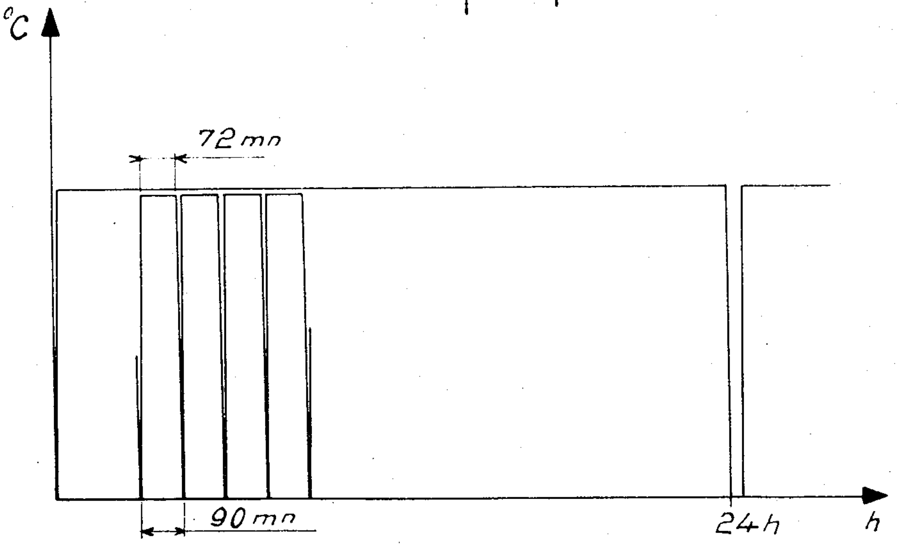

Fig. 2

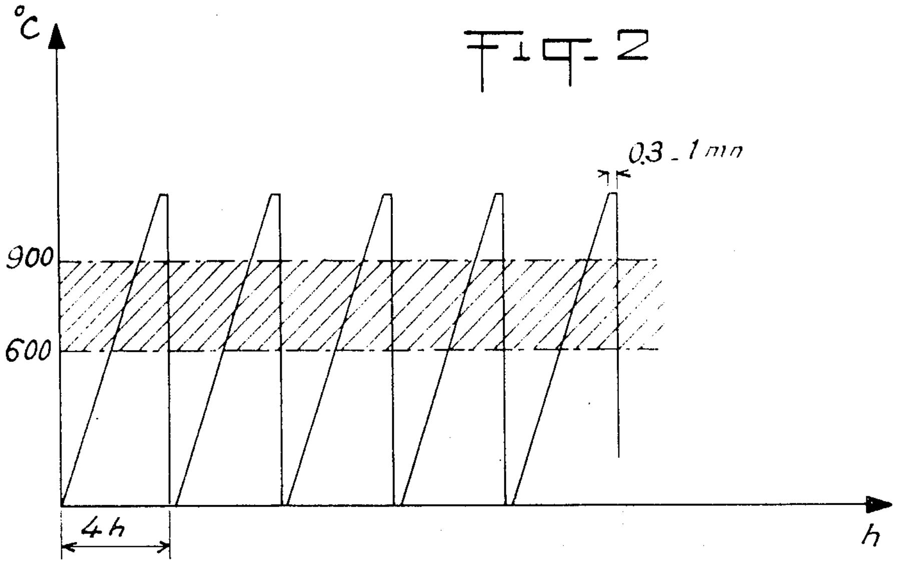

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Fig. 3

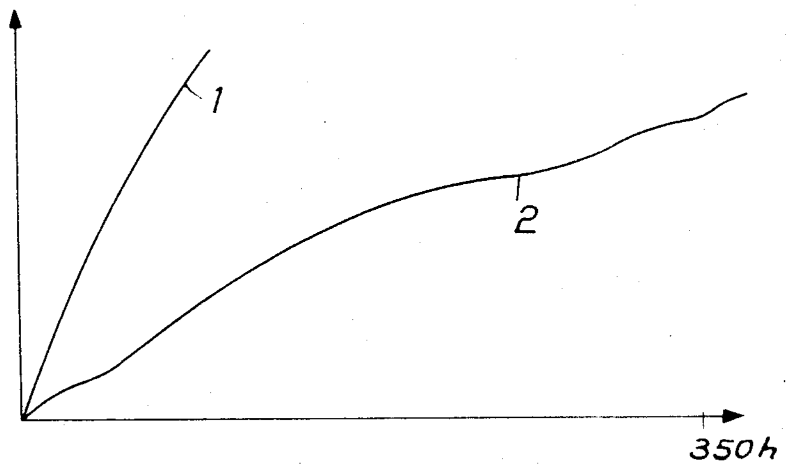
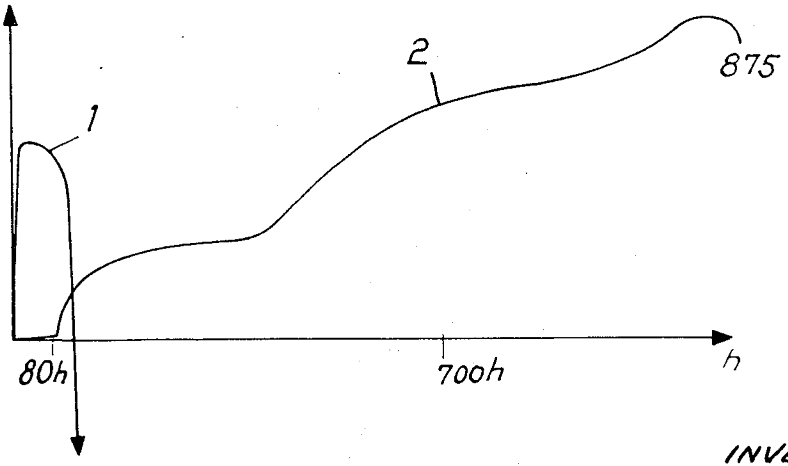


Fig. 4



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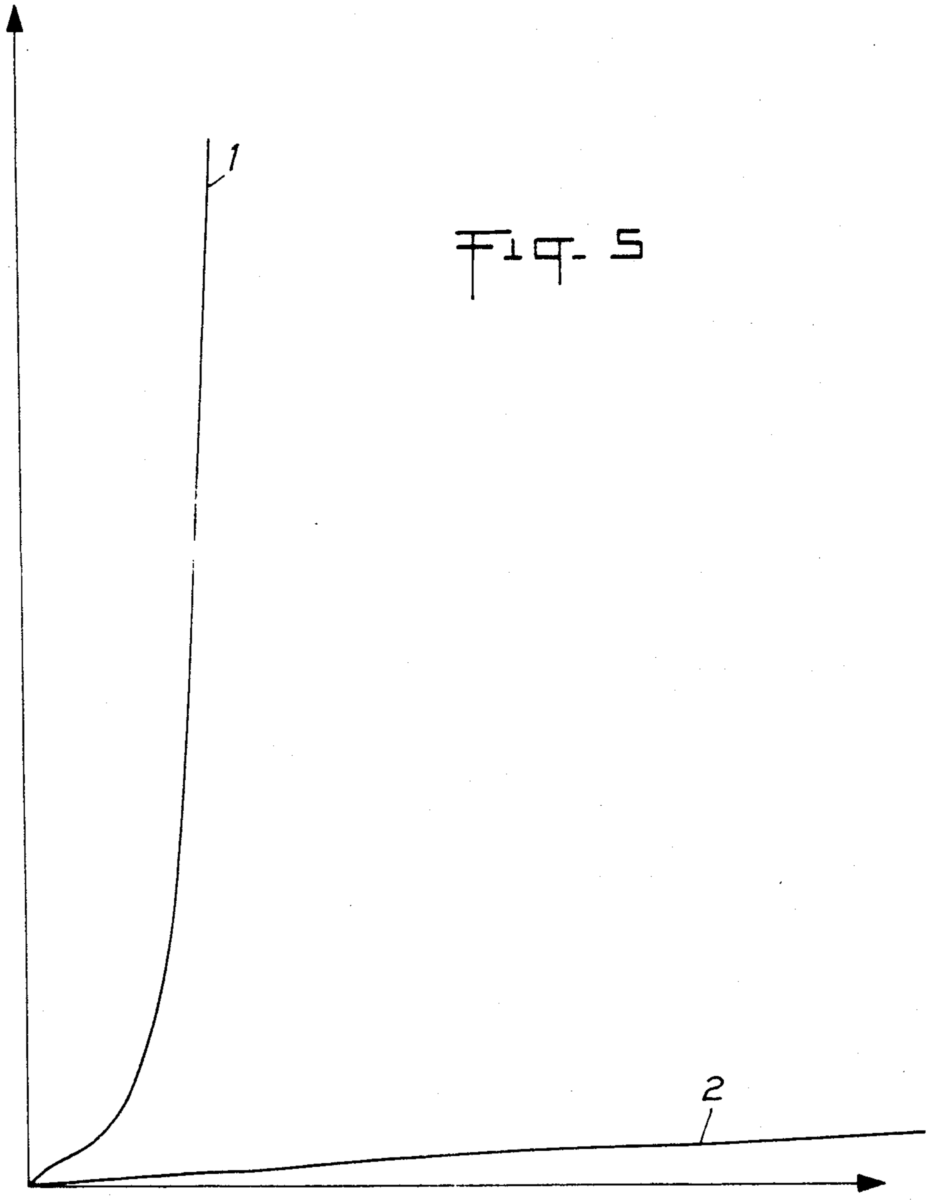

Fig. 5

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NIOBIUM-BASED OXIDATION RESISTANT MATERIALS AND PROCESS FOR THEIR PREPARATION

The present invention concerns a procedure for improving the hot oxidation resistance of niobium and niobium based alloys.

The use of niobium and niobium-based alloys poses considerable problems as regards the possibility of effective protection against oxidation of the work-pieces or their surfaces produced using these materials. Attempts have been made in practice to resolve these problems by depositing on the surface materials, metals, mixtures of metals, or metallic alloys or compounds which can be made to adhere to the underlying material by heating in vacuum or in a neutral or reactive atmosphere at a high temperature. These metals or alloys form a thin protective layer which to some degree ensures protection of the underlying material against the oxidation which can develop after utilisation of the pieces at high temperature.

But it has been recognised, and systematic tests have confirmed, that the protection thus achieved is always insufficient, more particularly when these pieces are submitted to successive thermal cycles with relatively slow rise of temperature followed by thermal shock. The pieces are destroyed always according to the same process known to specialists under the name of "plague" and which is made evident by the appearance of swellings on the surface on the said pieces. These swellings, distributed at random, result in very rapid destruction of the protective layer and a later rapid destruction of the piece itself.

According to French Pat. No. 1,305,861 a process has been proposed of protecting pieces made of niobium or niobium alloys, in which a coating is deposited on the surface of the said pieces and is constituted by a metal or a metalloid capable of giving a refractory substance, the product thus obtained is subjected to annealing, and the sintered layer thus formed is oxidized. Among the metals and metalloids which are suitable, aluminium and its alloys, silicon and its alloys, and chromium and its alloys have been cited.

This procedure however has the inconvenient feature of not producing a sufficiently durable protection for the niobium or niobium alloy workpieces, particularly as regards successive thermal shocks to which they are submitted.

There has also been proposed in French pat. No. 1,438,749 a process of protecting pieces made of niobium or niobium alloys containing at least 50 percent by wt. of niobium, according to which the said pieces are coated with a mixture comprising on the one hand silicon, on the other hand vanadium and/or manganese, and also at least three elements chosen from tantalum, niobium, tungsten, molybdenum, chromium, titanium, zirconium, aluminium and boron. After heating under vacuum or in an argon atmosphere, and oxidation for 1 to 3 hours, the obtained pieces however cannot sustain successive thermal shocks for more than 250 hours.

The present invention has as its object a solution of the problem of the oxidisability of pieces made of niobium and niobium alloys, and a reduction of the disadvantages of the prior art. It thus concerns, as regards new materials, pieces made of niobium or alloys of niobium coated, according to known processes, by so-called protective coatings with a metal or metallic alloy base forming, with the niobium or niobium alloy underlying it, associations or alloys of niobium silicide or aluminide type characterised in that the superficial zone of the protective layer contains at least 70 percent by wt. of metallic oxides of type $(Nb, M_1, M_2, M_3, \ldots M_n)_2O_5 = (M_1, M_2, M_3, \ldots M_n =$ metals constituting the alloy or the protection which substitute for niobium in the complex β-form oxide).

The invention is based on the following scientific observations:

the metallic oxides of niobium of the β-Nb_2O_5 type are thermally stable and the transformation $\alpha \rightarrow \beta$ is irreversible;

certain complex oxides of niobium of β-$(Nb, M_1, M_2, M_3, \ldots M_n)_2O_5$ type form a protective barrier effective at high or low temperature against oxygen;

the metallic oxides of niobium of the β-$(Nb, M_1, M_2, M_3, \ldots M_n)_2O_5$ type can be prepared by oxidising the superficial protective coating without dislodging it as long as one operates in conditions where the oxides formed, in particular the oxides of α-$(Nb, M_1, M_2, M_3, \ldots M_n)_2O_5$ type transform into oxides of the β-$(Nb, M_1, M_2, M_3, \ldots M_n)_2O_5$ type to the same extent as they are formed.

The application of these various observations to the protection of niobium or of its alloys thus leads to depositing on the surface of pieces of niobium, or of its alloys, certain elements, themselves known, based on metals or alloys; producing, by heating under vacuum or neutral or reactive atmosphere and according to known processes, the associations or alloys of niobium with the deposited elements so as to form derivatives of the alloyed niobium silicide or aluminide type; then treating by oxidation the piece thus obtained in conditions such that the superficial layer of silicide or aluminide type thus created is transformed into a metallic oxide of β-$(Nb, M_1, M_2, M_3, \ldots M_n)_2O_5$ type. This oxidation of the superficial layer should be effected without oxidation of niobium or of the alloy of niobium which is situated below this layer; this result can be obtained by effecting the oxidation reaction in conditions such that the speed of transformation of metallic oxides of the α-$(Nb, M_1, M_2, M_3, \ldots M_n)_2O_5$ type into metallic oxides of the β-$(Nb, M_1, M_2, M_3, \ldots M_n)_2O_5$ type is at least equal the speed of formation of the metallic oxides of the α-$(Nb, M_1, M_2, M_3, \ldots M_n)_2O_5$ type.

This condition can be expressed in another way by saying that during the oxidation reaction the proportion of metallic oxides of α-$(M_1, M_2, \ldots M_n)_2O_5$ type in the protective layer should always be low.

When the operating conditions indicated above are followed, the "protection surface" is oxidised without penetration of oxygen into the niobium or niobium alloy beneath.

The invention thus concerns a procedure for preparation of pieces of new material, as defined above, characterised in that the said pieces, previously treated according to known processes for formation of superficial metallic protective layers, are subjected to an oxidation reaction under operating conditions in which the speed of formation of the metallic oxides of β-$(Nb, M_1, M_2,$ Mhd 3, $\ldots M_n)_2O_5$ type from the metallic oxides of α-$(Nb, M_1, M_2, M_3, \ldots M_n)_2O_5$ type is greater than the speed of formation of the metallic oxides of α-$(Nb, M_1, M_2, M_3, \ldots M_n)_2O_5$ type.

This oxidation reaction should be effected while maintaining the material, coated with a metallic layer which is in itself known, in air at atmospheric pressure at a temperature between 700° and 1,200°C for a time exceeding 50 h and, preferably, for 50–300 h according to the composition of the layer. Preferably, also, the treatment is conducted in still air, at a temperature between 700° and 900°C.

For a good understanding of the above, what is meant by metallic oxides of type α or β should be explained. It is known that oxidation of niobium in air, at high temperature, leads to solution of oxygen in the niobium and the simultaneous formation in the surface of oxides of which the principal are NbO, NbO_2, Nb_2O_5. Niobium pentoxide Nb_2O_5 can occur in two different crystalline forms; one orthorhombic form, α, and one monoclinic, β. According to the invention, a thin layer of metal alloys is deposited on the surface of the niobium or the niobium alloy to be protected. For example, a paint containing nickel, titanium, chromium, and aluminium is deposited on the surface of the niobium. By later heating in vacuum, there is a chemical reaction between these metals and the underlying niobium with formation of chemical compounds containing niobium. For example, alloyed niobium aluminide will be formed. When, according to the invention, this superficial layer is subjected to oxidation, the atoms of niobium will oxidise as welll as the other metallic atoms, leading to the formation of various oxides. For example, there can form the α or β form of $(Nb, M_1, M_2, M_3, \ldots M_n)_2O_5$. By definition, we have termed the metallic oxide of β-$(Nb, M_1, M_2, M_3, \ldots M_n)_2O_5$ type the oxidation state of this superficial layer, for which the quasi-totality of the atoms of niobium is in the form of Nb_2O_5, and for which the crystalline structure of the said superficial layer is monoclinic, that is, identical or similar to the crystalline form of β-niobium pentoxide.

According to a preferred mode of procedure, the protective layer of β type $(Nb, M_1, M_2, M_3, \ldots M_n)_2O_5$ oxides is obtained by depositing on the surface of the piece made of niobium or niobium alloys a powder comprising at least three of the following elements, Si, Al, Cr, Fe, Ti, Ni and Co, and subjecting the piece thus coated to a controlled oxidation in the conditions given above.

The powder contains, according to one characteristic of the invention, silicon or aluminium, the silicon or aluminium being always associated with niobium and chromium, the fourth constituent being chosen among the remaining metals of the list given above, i.e., iron, titanium, nickel and cobalt. The preferred powders are those comprising:

a. a mixture of Si, Cr, Fe,
b. a mixture of Si, Cr, Ti,
c. a mixture of Al, Cr, Ti,
d. a mixture of Al, Cr, Ni, Ti and
e. by the mixtures obtained by incorporating cobalt in each of the powders *a*, *b*, *c* and *d*.

In these powders the quantities of Si or Al are equivalent, the said quantities being considerably greater than those of Cr, Fe, Ti, Ni and Co. In general one can use by weight:

50 parts of Si or Al
1 part of Cr
1 part of Fe, Ni, Ti and/or Co.

The non-limitative trials below illustrate the invention. The results of these trials can be better understood by referring to FIGS. **1** to **5**.

FIGS. **1** and **2** relate to modes of heating of the pieces during the tests carried out (the ordinate gives temperature, the abscissa gives time).

FIGS. **3**, **4** and **5** show the comparative speed of oxidation of samples, treated according to the invention, or untreated; FIG. **3** gives the results obtained with isothermal heating; FIGS. **4** and **5** the results obtained with cyclic heating. For these figures the ordinate gives the variation of weight of the sample and the abscissa gives the time.

These tests have been carried out by subjecting the treated or untreated samples to thermal cycles; these thermal cycles are of two types: type A, in which the samples are kept during considerable times at high temperature, or type C in which the samples are not kept for a long time at a high constant temperature.

The type A cycle consists in keeping the sample isothermally for a longer or shorter time at the maximum test temperature, which is usually between 1,000°C and 1,400°C, with the heating to temperature and the cooling to ambient temperature effected rapidly enough, that is in a time between several seconds and several minutes. FIG. **1** shows schematically two cycles of this type, a cycle A of 90 minutes duration and a cycle A′ of 24 hours' duration.

The type C cycle is as follows: a slow rise to the test temperature, holding for a short time and rapid cooling. FIG. **2** shows schematically a type C cycle of 4 hours duration, where the rate of temperature rise is 300°C per hour approximately.

If the life times are compared of an ordinary sample of niobium, obtained with the two types of test, it is observed that for a same maximum test temperature, fixed in this case at 1,100°C, and in spite of a holding time equal to 85 percent of the test duration with cycle A, of 90 minutes duration against only 2 to 3 for cycle C, of 4 hours duration, that is about 30 times shorter duration, the life time is however divided by a factor of the order of 10 to 20 when one passes from cycle A to cycle C.

EXAMPLE 1

FIG. **3** shows the difference between the speed of oxidation at a constant temperature of 700°C between Sample 1, which had not undergone the previous treatment according to the invention, and Sample 2, which had undergone a previous treatment of 140 hours at 900°C. These two samples were protected by a mixture of powder based on silicon-chromium-iron of about 0.15 mm thickness. This example is to show the improvement obtained during prolonged maintenance in the dangerous temperature zone.

EXAMPLE 2

FIG. **4** shows the gain in weight of two samples during an oxidation test according to a cycle of type C with a maximum temperature of 1,100°C. The **2** samples had simultaneously received the same protection by a mixture of powders based on Si-Cr-Fe, but sample number 1 was tested as it was, while sample number 2 was additionally subjected to a controlled thermal oxidation and aging treatment of 200 hours at 900°C. Final failure, characterised by a considerable fall in weight, is shown around 80 hours for sample number 1 and at 875 hours for sample number 2, which represents an improvement factor of the order of 10.

EXAMPLE 3

Two samples protected by a deposit of type Si-Cr-Fe of about 0.15 mm thickness were tested as in the example above, following cycle C at 1,100°C, and gave the following results:

- the first non treated sample had a life time of 10 hours;
- the second sample, having received a previous controlled thermal oxidation and ageing treatment according to the invention of 240 hours at 900°C in air, at atmospheric pressure, had a life time of 300 hours.

The application of the treatment thus gave, in this case, a multiplication by 30 of the life time.

EXAMPLE 4

FIG. 5 permits examination of the gains in weight obtained in oxidation tests following a type A cycle at 800°C with durations of 24 hours. The weight gain was obtained by weighing after each period. The samples of niobium alloy were protected by a coating of 0.03 mm comprising chromium, titanium, and aluminium deposited in the vapour phase. Sample number 1 was untreated, but sample number 2 had undergone a controlled thermal oxidation and aging treatment of 264 hours at 700°C. A spectacular difference is seen between the two tests, sample number 1 being rapidly destroyed and sample number 2 being still intact at the end of 792 hours of testing.

EXAMPLE 5

This example is given to show the importance of not exceeding 900°C, this temperature constituting the approximate limit above which the oxidation rate of niobium and the elements associated with it into a α-type Nb_2O_5 become prohibitive for the control of the process.

Two sets of test pieces were coated using a powder of Si, Cr, Fe. In each set the test pieces were either subject to a preliminary oxidation at atmospheric pressure in still air, or were not subject to the said oxidation. The life time according to cycle C is shown in Table 1 below.

TABLE 1

RESULTS OF TESTING WITH TWO SETS OF TEST PIECES PROTECTED BY SYLVANIA USING A DEPOSIT OF Si-Cr-Fe

Preliminary Oxidation (Atmospheric Pressure) medium: still air	Life time (h) in cycle C at 1100°C	Set. No.
untreated	60	1
untreated	130	1
3 h at 1100°C	178	1
15 h at 1100°C	210	1
195 h at 900°C	875	1
195 h at 900°C	905	1
untreated	8	2
untreated	12	2
237 h at 1100°C	300	2

We claim:

1. Niobium or a niobium-based alloy having a protective coating formed of mixed metalic oxides of the β-$(Nb, Me)_2O_5$ type, wherein Me includes a metal having a major amount of aluminum or silicon alloyed with chromium and at least one other metal taken from the group consisting essentially of iron, titanium, nickel, cobalt, or mixtures thereof.

2. Niobium or a niobium-based alloy according to claim **1** wherein said protective coating comprises at least 70 percent by weight of mixed metallic oxides of the Beta form. c

3. Niobium or a niobium-based alloy according to claim **2** are 50 parts aluminum and/or silicon to 1 part each of chromium, iron, nickel, titanium and/or cobalt.

4. Niobium or a niobium-based alloy according to claim **1,** wherein the protective coating composition is taken from the group comprising the following combination of metals:

Si, Cr, Fe;
Si, Cr, Ti;
Al, Cr, Ti;
Si, Cr, Fe, Co;
Si, Cr, Ti, Co;
Al, Cr, Ti, Co; or
Al, Cr, Ni, Ti, Co.

5. Process for the manufacture of niobium or a niobium-based alloy comprising the steps of forming a protective coating of the $(Nb, Me)_2 O_5$ type wherein Me includes a metal having a major amount of aluminum or silicon alloyed with chromium and at least one other metal taken from the group consisting essentially of iron, titanium, nickel, cobalt, or mixtures thereof; heating and oxidizing said $(Nb, Me)_2O_5$ layer at 700° to 1,200°C for a time sufficient to convert a major portion of said layer to the β-oxide form.

6. The process according to claim **5** wherein said protective layer is heated in air at 700°C to 900°C for at least 50 hours.

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