# United States Patent [19]

Horiuchi et al.

[11] **3,867,209**

[45] **Feb. 18, 1975**


[54] **METHOD OF TREATING Ti-Nb-Zr-Ta SUPERCONDUCTING ALLOYS**


[75] Inventors: **Takefumi Horiuchi**, Kobe; **Yoshiyiki Monju**, Nishinomiya; **Isamu Tatara**, Kobe; **Nobuyuki Nagai**, Kobe; **Manabu Hisata**, Kobe; **Kiyoshi Matsumoto**, Kobe, all of Japan

[73] Assignee: **Kobe Steel, Ltd.**, Kobe City, Japan



[22] Filed: **Sept. 17, 1973**

[21] Appl. No.: **397,866**

[52] **U.S. Cl.**............ **148/12.7,** 75/134 R, 75/134 N, 75/174, 75/175.5, 148/11.5 F, 148/32.5

[51] **Int. Cl.** ............................................. **C22f 1/18**

[58] **Field of Search**... 75/134 R, 134 N, 174, 175.5; 148/11.5, 12.7, 133, 32, 32.5



[56] **References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,822,268 | 2/1958 | Hix | 75/174 |
| 3,038,798 | 6/1962 | Berger et al. | 75/174 |
| 3,408,604 | 10/1968 | Toshio Doi et al. | 75/174 X |
| 3,671,226 | 6/1972 | Komata et al. | 75/174 |

FOREIGN PATENTS OR APPLICATIONS

| | | | |
|---|---|---|---|
| 243,841 | 10/1969 | U.S.S.R. | 75/175.5 |

OTHER PUBLICATIONS

Journal of Applied Physics, Vol. 38, 1967, page 903 and 904.

Superconducting Materials, Savitskii et al., Plenum Press, N.Y. 1973, pages 350 and 351.



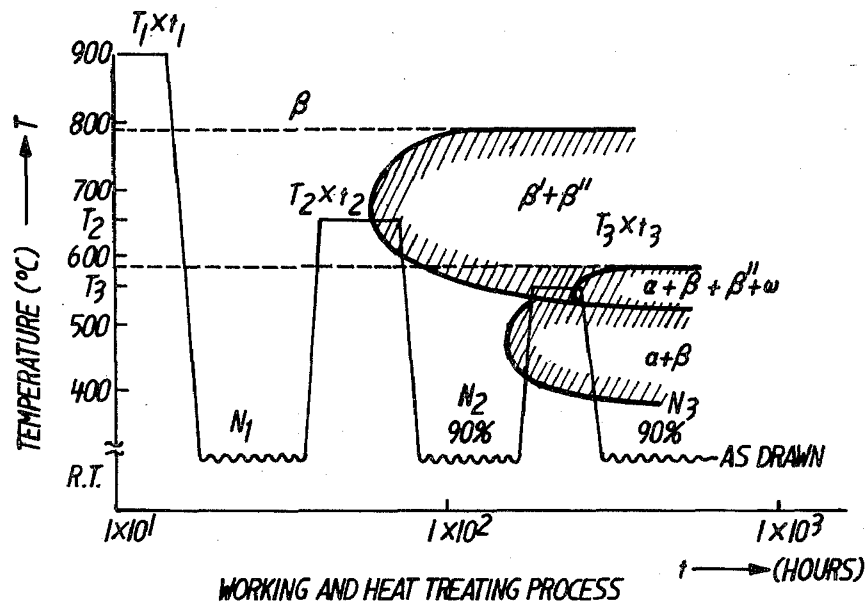
*Primary Examiner*—C. Lovell

*Attorney, Agent, or Firm*—Oblon, Fisher, Spivak, McClelland & Maier


[57] **ABSTRACT**


A superconducting metal alloy is formulated from 10–50 at % Ti, 20–50 at % Nb, 10–40 at % Zr and 5–12 at % Ta. A Ti-Nb-Zr-Ta superconducting alloy with a fine, non-homogeneous structure is obtained by forming a $\beta$ solid solution of said Ti-Nb-Zr-Ta alloy by heating the alloy to a temperature within the $\beta$ solid solution range, cooling and then cold working said heated alloy, heating said cold worked alloy to a temperature within the ($\beta'$+$\beta''$) alloy to maintain the peritectoid structure, cold working the peritectoid alloy, heating said peritectoid alloy to a temperature within the eutectoid range to form a multiphase eutectoid alloy structure and then cooling said eutectoid alloy and finally cold working the eutectoid alloy.


**1 Claim, 8 Drawing Figures**



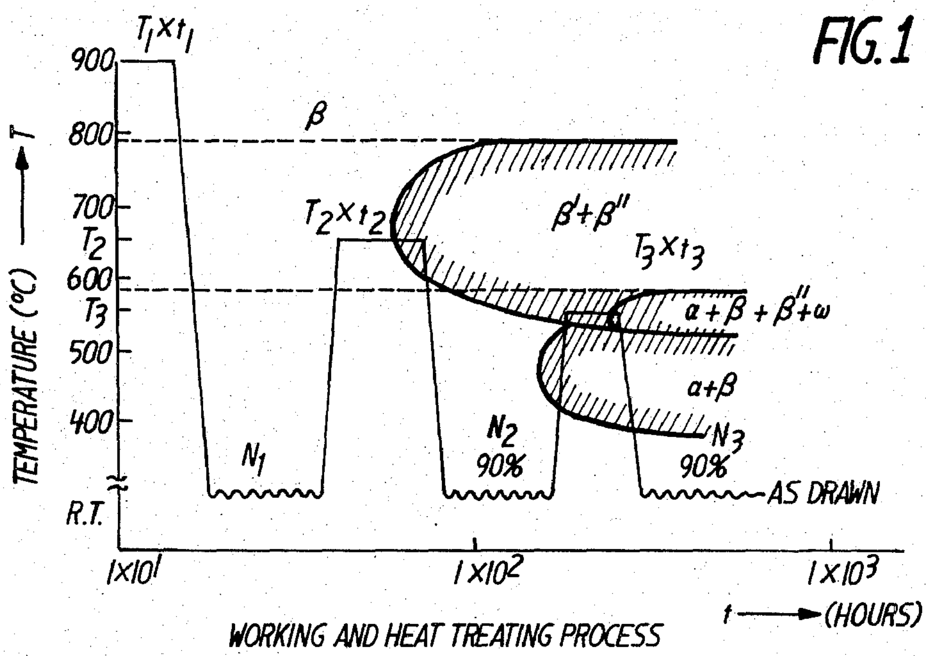

$T_1 \times t_1$
900
800
700
$T_2$
600
$T_3$
500
400
R.T.
β
$T_2 \times t_2$
β′+β″
$T_3 \times t_3$
α+β+β″+ω
α+β
$N_1$
$N_2$
90%
$N_3$
90%
AS DRAWN
TEMPERATURE (°C) → T
1×10¹
1×10²
1×10³
t → (HOURS)
WORKING AND HEAT TREATING PROCESS

FIG. 1

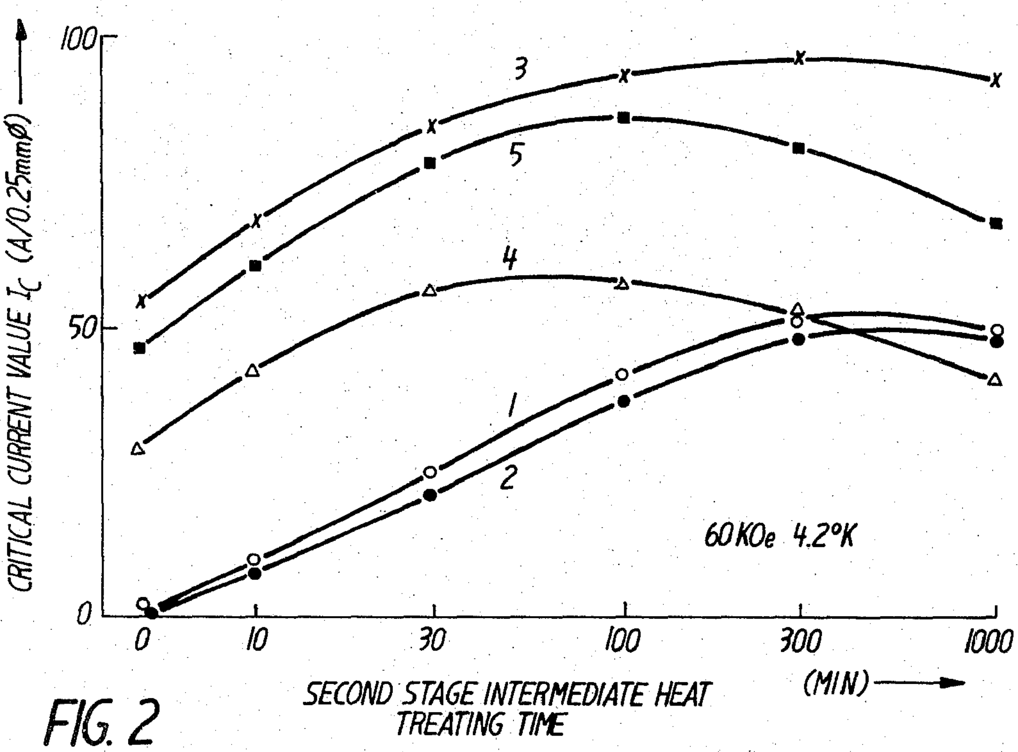

100
50
0
CRITICAL CURRENT VALUE $I_C$ (A/0.25mmØ) →
3
5
4
1
2
60KOe 4.2°K
0
10
30
100
300
1000
(MIN) →
SECOND STAGE INTERMEDIATE HEAT TREATING TIME

FIG. 2

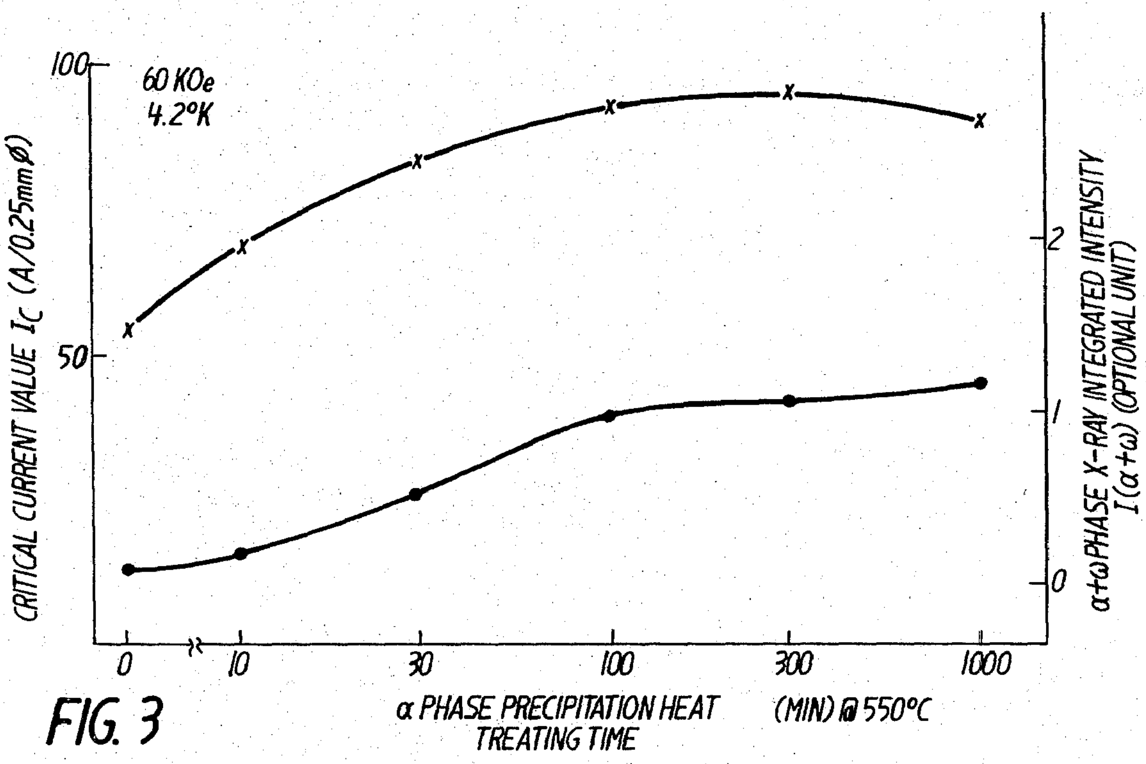

100
50
60 KOe
4.2°K
CRITICAL CURRENT VALUE $I_C$ (A/0.25mm ø)
0
1
2
α+ω PHASE X-RAY INTEGRATED INTENSITY
I(α+ω) (OPTIONAL UNIT)
0
10
30
100
300
1000
α PHASE PRECIPITATION HEAT TREATING TIME
(MIN) @ 550°C

FIG. 3

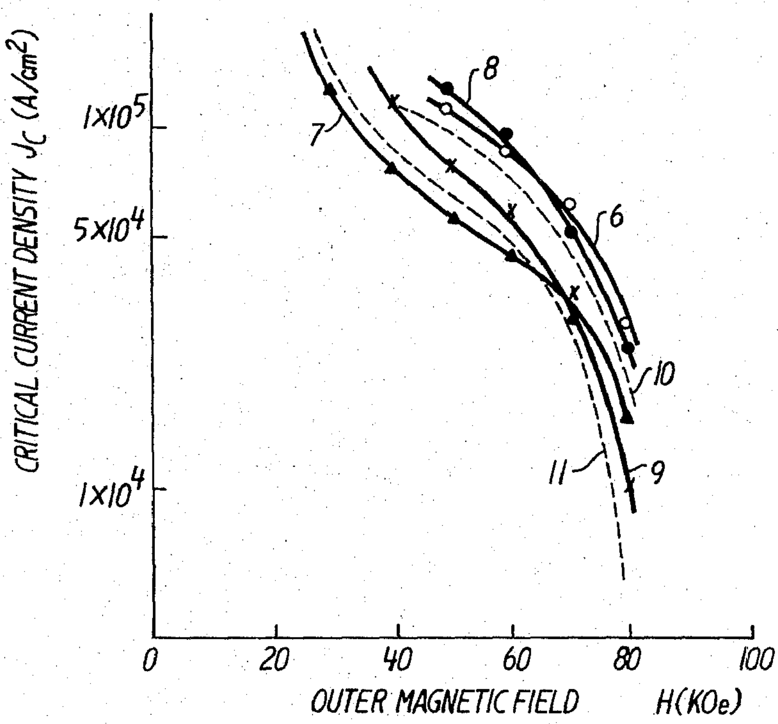

CRITICAL CURRENT DENSITY $J_C$ (A/cm²)
1×10⁵
5×10⁴
1×10⁴
6
7
8
9
10
11
0
20
40
60
80
100
OUTER MAGNETIC FIELD
H(KOe)

FIG. 4

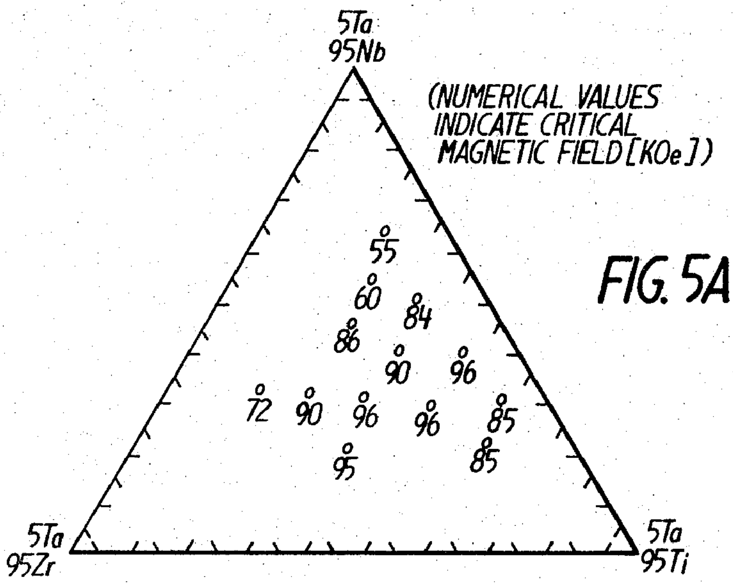
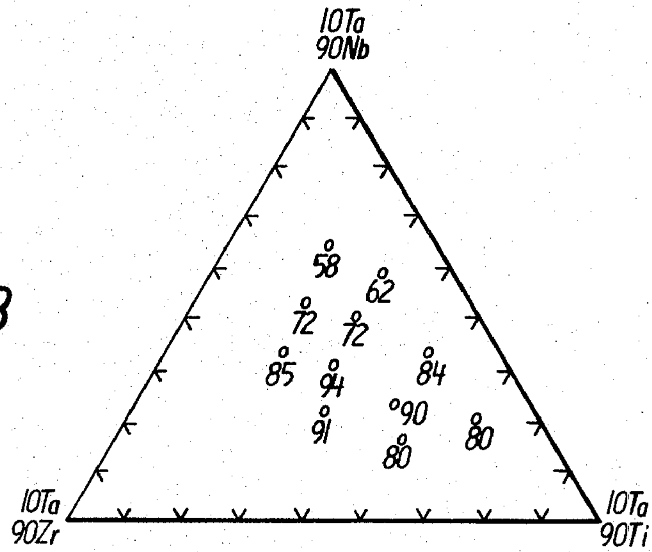

5Ta
95Nb
(NUMERICAL VALUES
INDICATE CRITICAL
MAGNETIC FIELD [KOe])
55
60
84
86
90
96
72
90
96
96
85
95
85
5Ta
95Zr
5Ta
95Ti

FIG. 5A

FIG. 5B


10Ta
90Nb
58
62
72
72
85
94
84
90
91
80
80
10Ta
90Zr
10Ta
90Ti

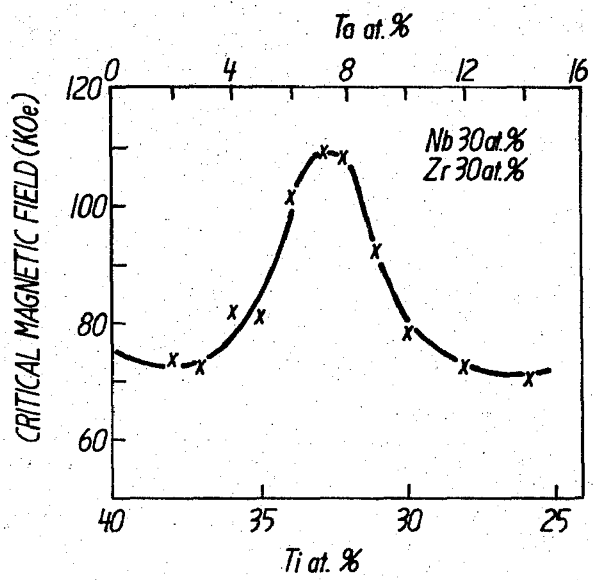
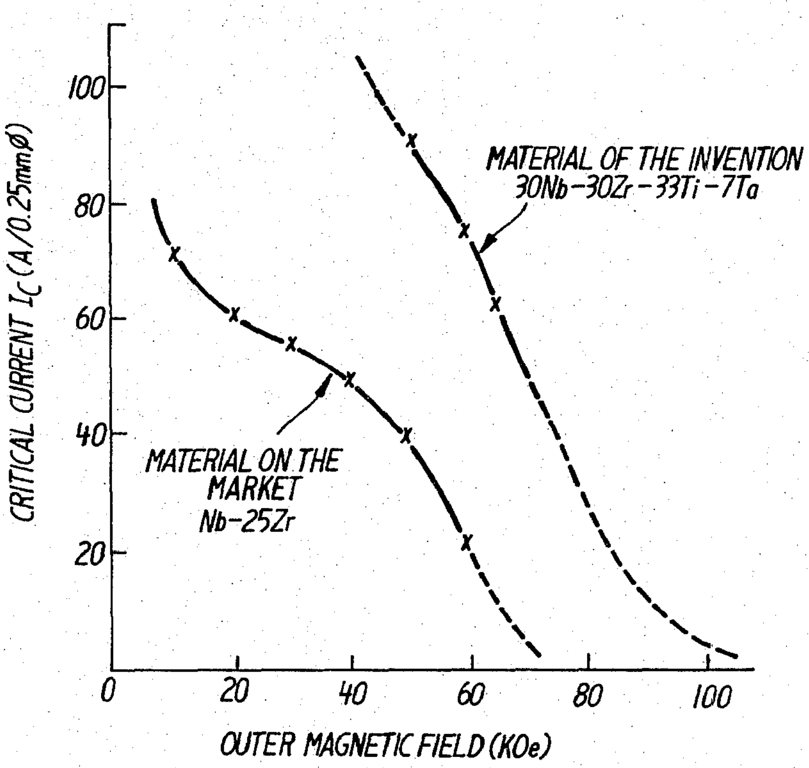

Ta at.%
0
4
8
12
16
120
100
80
60
CRITICAL MAGNETIC FIELD (KOe)
Nb 30at.%
Zr 30at.%
40
35
30
25
Ti at. %

FIG. 6

FIG. 7


100
80
60
40
20
CRITICAL CURRENT $I_C$ (A/0.25mmØ)
MATERIAL OF THE INVENTION
30Nb-30Zr-33Ti-7Ta
MATERIAL ON THE
MARKET
Nb-25Zr
0
20
40
60
80
100
OUTER MAGNETIC FIELD (KOe)

# METHOD OF TREATING Ti-Nb-Zr-Ta SUPERCONDUCTING ALLOYS

## BACKGROUND OF THE INVENTION

### Field of the Invention

The present invention relates to superconducting alloys. More particularly, the present invention relates to a method of working and treating a non-homogeneous superconducting Ti-Nb-Zr-Ta alloy.

### Description of the Prior Art

Superconducting alloys formed from Ti-Nb, Nb-Zr and Ti-Nb-Zr mixtures are well known. The critical current density, Jc, of these superconducting alloys can be increased by various known techniques, such as for example, a final low temperature aging treatment after strong working of the Ti-Nb alloys, a strong working treatment of the Nb-Zr alloys and a multi-phase heat treatment of the Nb-Zr-Ti alloys. Japanese Patent application Publication No. 14,028/68 has proposed a multi-phase heat treatment for Ti-Nb-Zr alloys. This treatment has the disadvantage that when it is desired to conduct a multi-phase heat treatment in the working process as an intermediate heat treatment, the density Jc at low magnetic fields is low. If, however, it is desired to use the multi-phase heat treatment in the final heat treatment stage, the density Jc of the medium and the high magnetic fields of the alloys decrease. Further, the optimum heat treatment temperature for multi-phase heat treating the Ti-Nb-Zr alloys is a relatively high temperature of about 700°C. When operating at these temperatures, however, certain percautions must be taken. That is, these kinds of superconducting alloys are coated with copper after the $\beta$ solid solution treatment, and then worked and heat treated. During the heat treatment at temperatures greater than 700°C, a reaction between the superconducting alloy and the copper coating occurs which produces certain undesirable results. Thus, the multi-phase heat treatment when used on these alloys should be conducted before being coated with copper.

Other conventional superconducting materials have also been known, such as the solid solution alloys of Ti-Nb, Nb-Zr, and Ti-Nb-Zr as well as compounds such as $Nb_3Sn$, $V_3Ga$, NbN, and the like. These superconducting alloy compositions have various advantages and disadvantages. For example, the Ti-Nb alloy has a relatively high critical magnetic field (about 120 KOe), but when its external magnetic field is less than 40 KOe, the critical current value thereof is not very substantial. On the other hand, the Nb-Zr alloy has a large critical current value at magnetic fields less than 40 KOe in relation to the external magnetic field. However, the critical current value is small when the critical magnetic field is less than 70 KOe. Furthermore, the critical magnetic field and the critical current of these superconducting compounds are excellent, but the technique of manufacturing these materials is difficult and expensive.

A need, therefore, continues to exist for a superconducting alloy which is more readily and less costly produced while simultaneously having excellent superconducting characteristics from low to high magnetic fields.

## SUMMARY OF THE INVENTION

Accordingly, one object of the present invention is to provide a method for treating superconducting alloys which gives alloys which have excellent superconducting characteristics at low magnetic fields as well as the medium and high magnetic fields.

Another object of the present invention is to provide a method for treating superconducting alloys to provide alloys which have excellent workability and mechanical properties.

Yet another object of the present invention is to provide a superconducting alloy which has excellent superconductivity, workability and mechanical characteristics at low magnetic fields as well as at medium and high magnetic fields.

Briefly, these objects and other objects of the present invention as hereinafter will become more readily apparent can be attained by providing a Ti-Nb-Zr-Ta alloy with a fine, non-homogenous structure by forming a solid solution of the Ti-Nb-Zr-Ta alloy by heating the alloy to a temperature within the $\beta$ solid solution range, cooling and then cold working the heated Ti-Nb-Zr-Ta alloy, heating the cold worked alloy to a temperature within the $(\beta'+\beta'')$ phase region and then cooling the heated $(\beta'-\beta'')$alloy to maintain the peritectoid structure, cold working the peritectoid alloy, forming a multiphase $\beta'+\beta''+\alpha(\omega)$ eutectoid alloy structure by heating the peritectoid alloy to a temperature within the $(\beta'+\beta''\rightarrow\beta'+\beta''+\alpha(+\omega))$ eutectoid structure range and then cooling the eutectoid alloy and cold working the eutectoid alloy. A Ti-Nb-Zr-Ta superconducting alloy is also provided which comprises 10–50 at % Ti, 20–50 at % Nb, 10–40 at % Zr and 5–12 at % Ta.

## BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

FIG. 1 is a diagram showing a T.T.T. curve of a 90% cold worked Ti-30 at % Nb-30 at % Zr-7 at % Ta alloy;

FIG. 2 is a diagram which shows the influence of the phase separation heat treatment time on the two phase heat treatment as a parameter of the critical current value of the Ti-30 at % Nb-30 at % Zr-7 at % Ta alloy;

FIG. 3 is a diagram which shows the influence of the $\alpha$ phase precipitation heat treatment time to the X-ray integrated intensity of the $\alpha$ phase and the $\omega$ phase of the Ti-30 at % Nb-30 at % Zr-7 at % Ta alloy, and to the critical current value;

FIG. 4 is a diagram which shows a comparison of the H—Jc curves of a conventional Nb-Zr-Ti alloy and the Ti-30 at % Nb-30 at % Zr-7 at % Ta alloy of the present invention;

FIG. 5 is a diagram which shows the superconducting characteristics, i.e., the critical magnetic field, of various Ti-Nb-Zr-Ta quaternary alloys;

FIG. 6 is a diagram which shows the superconducting characteristics i.e., the critical magnetic field of a quaternary alloy containing 30 at % Nb and 30 at% Zr in which the Ti and Ta content is continuously changed; and

FIG. 7 is a diagram which shows the realtion between the external magnetic field and the critical current value of a material of the present invention in comparison to the relationship of the same properties of another conventionally available superconductiong alloy.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. 1 shows the T.T.T. curve of a 90% cold worked Ti-30 at % Nb-30 at % Zr-7 at % Ta superconducting alloy, which is just one of the Ti-Nb-Zr-Ta superconducting alloys of the invention as determined by X-ray analysis and an electrical resistance method. As shown, the upper temperature limit of the $\beta'+\beta''$ region is about 775°C and the upper limit of the $\beta'+\beta''\rightarrow\beta'+\beta''\alpha(+\omega)$ region is about 580°C. As can also be seen, the peritectoid temperature region and the temperature region for the precipitation of the $\alpha$ phase and the $\omega$ phase of the Ti-Nb-Zr-Ta alloy decrease when Ta is added to the alloy in comparison to the Ti-Nb-Zr alloy. This occurs because Ta has an inhibiting effect on the $\alpha(+\omega)$ phase precipitation, which results in a delay in the precipitation of the $\alpha(+\omega)$ phase separation and the peritectoid region is enlarged. This observation is essential for the development of the heat treatment of the present invention. In the treatment of the metal the peritectoid heat treatment, which has not been performed, and the $\alpha$ phase precipitation heat treatment are independently conducted. The peritectoid heat treatment is conducted for a short period of time at a comparatively low temperature because of pre-working the alloy. The $\alpha$ phase precipitation heat treatment is conducted at a low temperature for only a short period of time by working, and the structure is finely refined and nonhomogenized. Further, in the $\alpha$ phase precipitation heat treatment, precipitation of the $\omega$ phase occurs. In particular, when the $\alpha$ phase precipitation heat treatment is conducted for only a short period of time, the $\alpha$ phase becomes an $\alpha$ $(+\omega)$ phase.

The present invention will be explained in more detail with reference to the working heat treatment depicted in the T.T.T. curve shown in FIG. 1.

The Ti-30 at % Nb-30 at % Zr-7 at % Ta alloy is first heated to a temperature in the $\beta$ region at a temperature higher than the peritectoid temperature (about 775°C), whereby a $\beta$ solid solution structure having uniform grains is formed. In this case, the treatment temperature $T_1$, and the treatment time $t_1$ are determined by the chemical composition of the alloy. However, within the $\beta$ phase region, a recrystallized region is preferably chosen where the crystal grains are comparatively finely maintained. A preferable treatment is to heat the alloy at a temperature $T_1$ of 850°–950°C and at a time $t_1$ of 1–5 hours. After the alloy is heat treated in the $\beta$ region, the sample is cooled, preferably quenched to maintain the $\beta$ solid solution structure. Thereafter, the cooled alloy is cold worked ($N_1$) which enables the peritectoid reaction, in the subsequent peritectoid ($\beta\rightarrow\beta'+\beta''$) heat treatment to be easily and thoroughly conducted. If the cold working step is not performed, the peritectoid in the grain boundary or the inner portions of the grain particles is not uniform. In order to prevent this nonumiformity and to promote the peritectoid reaction, the cold working step $N_1$ is performed at a working rate of more than 50%, perferably more than 90%.

After the alloy has been cold worked in the $N_1$ step, the alloy is heated within the $\beta'+\beta''$ region, whereby a peritectoid $\beta'+\beta''$ structure is achieved by decomposition of the solid solution $\beta$ structure. In this phase of the heat treatment in order to attain the peritectoid structure, there is not as great dependency between the



$T_2$ treatment temperature and the treatment time $t_2$ within the peritectoid region as in the case of the $\beta$ heat treatment. However, the treatment time $t_2$ largely depends on the preceding cold working $N_1$ step. Thus, the larger the $N_1$ step, the shorter the treatment time. If the treatment time $t_2$ takes longer, the superconducting characteristics of the alloy deteriorate. It is believed that the distance between the two phases is increased and the strain energy between the layer walls is reduced. The main point is that the treatment temperature and the time should be selected to maintain the peritectoid reaction in its latent period or initial stage, which can be determined by electrical resistance measurements, or by detecting changes in the X-ray pattern. The preferred peritectoid heat treatment is a temperature $T_2$ of 400°–700°C at a time $t_2$ of 1–5 hours. The peritectoid heat treatment is usually done once, but a more fine peritectoid structure can be made by repeating this treatment at least twice. In the peritectoid heat treatment, in order to improve the cold workability of the alloy for the subsequent cold working step, precipitation of the $\alpha$ phase by a eutectoid reaction ($\beta'\rightarrow\alpha+\beta''$) should be avoided. Further, in the precipitation heat treatment of the $\alpha$ phase in the final heat treatment step, in order to finely precipitate the $\alpha$ phase or the $\omega$ phase, the $\alpha$ $(+\omega)$ phase should not be present in the alloy which is to be treated in the $\alpha$ phase precipitation heat treatment step. If the $\alpha$ phase is present, the $\alpha$ phase grows during the $\alpha$ phase precipitation heat treatment and fine precipitation of the $\alpha$ phase cannot be attained, which means that the $\alpha$ $(+\beta)$ phase is never precipitated in the peritectoid heat treatment. All of this means that the earlier described limited heat treatment is necessary. Further, the cooling step after the peritectoid heat treatment is preferably a quenching step which maintains the peritectoid structure. The hardness of the alloy sample after the peritectoid heat treatment is slightly less when compared to the hardness of the sample after the cold working $N_1$ step and the workability is substantially improved.

The cold working step $N_2$ is performed to refine more thoroughly the two phase grain structure after the peritectoid heat treatment, and to provide a sufficient dislocation network to increase the number of $\alpha$ -phase precipitating nuclei from which grains grow when the next $\alpha$ phase precipitation heat treatment is conducted in order that the precipitation of the $\alpha$ $(+\omega)$ phase is easily and completely performed. The cold working step is conducted at a working rate of more than 50%, preferably more than 90%.

The final heat treatment step converts the alloy sample which has achieved the fine two phase separation structure to another structure by the $\alpha$ phase precipitation heat treatment. In the final heat treatment the fine $\beta'+\beta''$ peritectoid structure is converted to a fine $\beta'+\beta''+\alpha$ $(+\omega)$ multi-phase eutectoid structure. In the $\alpha$ phase precipitation heat treatment, the treatment temperature $T_3$ is not critical within the $\alpha$ phase precipitation region in relation to the treatment time $t_3$. However, the treatment time $t_3$ depends on the cold working of the preceding $N_1$ and $N_2$ steps, and the preceding peritectoid heat treatment ($T_2$, $t_2$). If the structure is sufficiently refined by the preceding cold working and heat treatment steps, the treatment time $t_3$ is decreased. If the treatment time $t_3$ is unnecessarily long, the superconducting characteristics of the alloy deteriorate. In the multi-phase separation heat treatment, the treatment temperature and the treatment time are also chosen such that the multi-phase separation reaction stops at the latent period or initial stage of the $\alpha$ phase precipitation. The preferred $\alpha$ phase treatment conditions are temperatures $T_3$ ranging from 450°–600°C and times $t_3$ of 1–5 hours. Further, this multi-phase separation heat treatment is usually performed once, but a more fine multi-phase separation structure can be achieved by repeating this treatment at least twice.

In order to provide the alloy with a finer non-homogeneous structure after the final $\alpha$ phase precipitation heat treatment, a cold working step $N_3$ is performed. This cold working step $N_3$ provides a finer alloy structure and also strengthens the dislocation networks at the non-homogeneous point to improve the superconducting characteristics (Ic characteristics). The cold working step $N_3$ is performed at a working rate greater than 50%, preferably greater than 90%.

By the process of the present invention, the Ti-Nb-Zr-Ta superconducting alloy, when subjected to the described working and heat treating procedures, is altered to a very fine multi-phase $\beta'+\beta''+\alpha(+\omega)$ separation structure which is non-homogeneous. By this procedure the superconductive characteristics (Ic characteristics) of the alloy material are improved.

The method of treatment of the present invention is applicable to superconducting alloys such as the quaternary Ti-Nb-Zr-Ta alloys. However, the chemical compositions of the alloy materials which are treated by the method of the present invention are limited by the different superconducting characteristics required of the superconducting alloys. These characteristics include transition temperature Tc, critical current value Ic, critical magnetic field Hcr, and the like. For instance, the presence of Nb in quantities less than 20 at % decreases the temperature Tc while the value Ic at the boiling point 4.2°K of liquid helium substantially deteriorates. If Nb is present in quantities less than 50 at % the Hcr value decreases which means that the Nb content of the alloy should be limited within 20–50 at %. If Zr is present in quantities less than 10 at %, the value of I shows no improvement, while if the Zr content is greater than 40 at %, the Hcr and Ic values and the cold workability of the alloy deteriorate. Thus, the Zr content is limited to values ranging from 10–40 at %. Ti shows no effect for the improvement of the Tc, Ic and Hcr values in quantities less than 10 at %, while in quantities greater than 50 at %, the Ic values deteriorate. Thus, the content of Ti should be within the range of 10–50 at %. Ta has an effect on the improvement of the Hcr and Ic values as well as the workability of the alloy. The presence of Ta makes it possible to carry out the method of the invention. When Ta is present in amounts less than 5 at %, no improvement in the Tc, Ic and Hcr values in quantities less than 10 at %, while in quantities greater than 50 at %, the Ic values deterio- and the Hcr values decrease. Thus, the Ta content is limited within the range of 5–12 at %.

Impurities, especially the interstitial impurities such as O, N, C, and the like, do not affect the superconducting characteristics of the alloy of the present invention. The impurities, however, to some extent have an effect on the mechanical properties of the alloy. When appreciable amounts of the impurities are present, the workability may deteriorate. However, when the impurity content of the alloy is of nominal levels, the characteristics of the alloy are not much affected.

The object of the present invention was to provide an alloy which has a relatively high critical magnetic field and a high critical current value at an external magnetic field less than 70 KOe. One of the features of the present invention is the Ti-Nb-Zr-Ta superconducting alloy which consists of 10–50 at % Ti, 20–50 at % Nb, 10–40 at % Zr, and 5–12 at % Ta and the usual impurities.

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

## EXAMPLE 1

The Ti-Nb-Zr-Ta alloys of the invention which have different compositions are melted and then manufactured into products. Any suitable method can be used for melting and manufacturing the alloy. However, according to the present invention, a sponge, powder, particle or the like mixture consisting of the desired Ti,Nb, Zr and Ta constituents is melted in a water cooled copper mold under an inert atmosphere by means of a tungsten arc lamp to form an ingot having a diameter of 15mm and a length of 40mm. The ingot is vacuum-sealed in a steel pipe and then hot forged. The forged ingot piece is drawn into a wire having a diameter of 0.25mm after annealing to provide a series of test pieces.

FIG. 5 (*a* and *b*) shows the value of the critical magnetic field measured for 0.25mm diameter test pieces of Ti-Nb-Zr-Ta quaternary alloys having different compositions which are subjected to a solution heat treatment for 5 hours at 1000°C in vacuum. In the measurement of the critical magnetic field of the alloy, a pulse magnetic field was applied at the temperature of liquid helium (4.2°K) and the magnetic field was measured under conditions in which the test pieces show normal conducting properties.

FIG. 6 shows the critical magnetic fields of the Nb-Ti-Zr-Ta quaternary alloys containing 30 at % Nb, 30 at % Zr and variously changing Ti and Ta contents.

It can be seen from FIGS. 5 and 6 that the Ti-Nb-Zr-Ta quaternary alloys within the range of the composition of the present invention show high critical magnetic fields. Particularly, it can be seen from FIG. 6 that when the Ta content is in the range between 5 and 12 at %, the critical magnetic field is substantially improved.

The alloy of the invention has improved superconducting characteristics as well as improved mechanical properties over the conventional alloys. That is, the Nb-Zr alloys and the Ti rich-Nb-Zr alloys have been known as alloys of low workability, but the alloys of the present invention have a cold workability of 99%, and are satisfactorily applicable under severe working conditions.

FIG. 7 shows the critical current value measured for a wire having a diameter of 0.25mm which is made of a superconducting alloy containing 33 at % Ti, 30 at % Nb, 30 at % Zr and 7 at % Ta which has been heat treated at 550°C for one hour after 90% cold working in each step and drawn into a wire. For purposes of comparison, a critical current value of a Nb-25Zr superconducting alloy in the form of a wire having a diameter of 0.25mm, which is commercially available on the market, is also shown. It can be seen that the alloy of the invention has a high critical current value in external magnetic fields less than 70 KOe.

The material of the present invention can be advantageously used for super-conductive magnet wires for MHD generators which is a new development in the energy industry; in coils of superconducting transformers or the like; and in the exciting coils of DC generators which makes it possible to compact the devices by increasing the exciting force by use of wires having a large critical current.

## EXAMPLE 2

A 100g amount of a mixture of Ti, 30 at %, Nb, 30 at % Zr and 7 at % Ta is melted by means of an arc to form an ingot having a diameter of 13mm. The ingot is vacuum-sealed in a steel pipe after being coated with a foil of Ta and then is hot forged. A number of rod shaped test pieces having a diameter of 7mm are formed by cutting the outer shell and the rod. The test pieces are heated to the $\beta$ phase region at a temperature of 850°C ($T_1$) for 2 hours ($t_1$) and then water quenched to form test pieces having the $\beta$ solid solution structure with a uniform grain. Then, the test pieces are cold swaged ($N_1$) into a wire having a diameter of 2.5mm (the working ratio is about 87%). The wire test pieces are then heat treated at three temperatures of 850°C, 650°C and 550°C ($T_2$) for 1–50 hours ($t_2$) and then water quenched. The temperature of 850°C is the $\beta$ phase region, the temperature of 650°C is the peritectoid region and the temperature of 550°C is the $\alpha$ (+$\omega$) phase region. Then, each of the test pieces is enclosed in an OFHC copper tube, and is cold drawn ($N_2$) to reduce the cross sectional area by 90% to form a wire having a diameter of 0.8mm. The drawn test pieces are heat treated at 550°C ($T_3$) for 0–1000 minutes ($t_3$) and then finally cold drawn ($N_3$) to reduce the cross sectional area by 90% to form a superconducting wire with a diameter of 0.25mm.

FIG. 2 shows the effect of the peritectoid treatment on the critical current value Ic of the prepared superconducting wire having a diameter of 0.25mm in an external magnetic field of 60 KOe at a temperature of 4.2°K. The histories of five test pieces Nos. 1–5 are shown in FIG. 2 and described in Table I.

TABLE I

| Test Piece No. | History of Test Pieces: Uniform grain $\beta$ phase treatment | Cold Working | First stage intermediate heat treatment |
|---|---|---|---|
| 1 | 850°C×2 hr | 87% | 850°C×2 hr |
| 2 | 850°C×2 hr | 87% | 850°C×50 hr |
| 3 | 850°C×2 hr | 87% | 650°C×3 hr |
| 4 | 850°C×2 hr | 87% | 650°C×50 hr |
| 5 | 850°C×2 hr | 87% | 550°C×3 hr |

| Test Piece No. | Cold Working | Second stage intermediate heat treatment | Cold working |
|---|---|---|---|
| 1 | 90% | 550°C×0-1000 min | 90% |
| 2 | 90% | 550°C×0-1000 min | 90% |
| 3 | 90% | 550°C×0-1000 min | 90% |
| 4 | 90% | 550°C×0-1000 min | 90% |
| 5 | 90% | 550°C×0-1000 min. | 90% |

As can be seen from FIG. 2, if the second stage intermediate heat treatment is conducted under the same conditions as the $\alpha$ phase precipitating heat treatment, the materials which have been treated by a first stage intermediate heat treatment at a temperature in the peritectoid region, i.e. at 650°C for 3 hours and for 50 hours, show higher critical current values than the materials treated in the $\beta$ phase region, i.e. at 850°C for 3 hours. Further, even if the first stage intermediate heat treatment of the alloy is conducted at a temperature in the peritectoid region, the heat treatment in the initial stage, i.e. at 650°C for 3 hours, shows higher critical current values than the alloys which have been heat treated under complete peritectoid conditions, i.e. at 650°C for 50 hours. Even if the first stage intermediate heat treatment is performed in the $\alpha$ phase precipitation region, i.e. at 550°C for 3 hours, a high critical current value is obtained for the alloy similar to the alloy heat treated at 650°C for 3 hours. However, the workability of the alloy is less so that further working is difficult. Therefore, it is desirable from the viewpoint of the critical current value and the workability that the first stage intermediate heat treatment be conducted in the peritectoid region, preferably for a short time.

FIG. 3 shows the relation between the critical current value and the X-ray integrated intensity I ($\alpha$+$\omega$) of the $\alpha$ phase and the $\omega$ phase for the second stage intermediate heat treatment (the $\alpha$ phase precipitation heat treatment) time ($t_3$) of test piece No. 3 of Table I. After the two phase separation heat treatment at 650°C for 3 hours, the $\alpha$ phase and the $\omega$ phase are not significantly present, but as the $\alpha$ phase precipitation heat treatment is prolonged, first the $\omega$ phase appears and then the X-ray integrated intensity of the $\omega$ phase increases. The X-ray integrated intensity I ($\alpha$+$\omega$) increases as the time passes, but the line profiles of the X-ray of the $\omega$ phase and the $\alpha$ phase extend largely in the initial stage of the precipitation. This means that the precipitates of the $\omega$phase and the $\alpha$phase are very fine. After the critical current values at a maximum of 550°C are obtained for 100 minutes, the line profile of the X-ray becomes sharp. Thus, it may be that the precipitated grains grow into an over aging condition. Therefore, it is desirable from the viewpoint of the inverse effect caused by the over aging action on the critical current value, that the precipitation of the grains in the $\alpha$ phase and the $\omega$ phase be satisfactorily controlled.

FIG. 4 shows the H—Jc characteristics of the Ti-30 at % Nb-30 at % Zr-7 at % Ta alloy of the invention and the known Nb-40 at % Zr-10 at % Ti alloy. Both alloys are treated with the uniform grain $\beta$ phase separation treatment at 850°C for 2 hours, the first stage intermediate heat treatment, a cold working step and the second intermediate heat treatment. The histories of the treated test pieces Nos. 6–11 are shown in FIG 4 and Table II.

TABLE II

History of Test Pieces

| Test Piece No. | Alloy (at%) | Uniform grain β phase treatment | Cold working | First stage intermediate heat treatment | Cold working |
|---|---|---|---|---|---|
| 6 | Ti-30Nb -30Zr- 7Ta | 850°C×2 hr | 87% | 650°C×1hr | 90% |
| 7 | | do. | do. | 650°C×3hr | do. |
| 8 | | do. | do. | do. | do. |
| 9 | | do. | do. | 650°C×50hr | do. |
| 10 | Nb-40Zr -10Ti | do. | do. | 650°C×3hr | do. |
| 11 | | do. | do. | do. | do. |

| Test Piece No. | Second stage intermediate heat treatment | Cold working |
|---|---|---|
| 6 | 550°C×100 min | 90% |
| 7 | — | do. |
| 8 | 550°C×100 min | do. |
| 9 | do. | do. |
| 10 | do. | do. |
| 11 | — | do. |

It is apparent from FIG. 4 that when the Ti-30 at % Nb-30 at % Zr-7 at % Ta alloy is treated in the peritectoid region at 650°C for 1–3 hours, is cold drawn in a reduction separation range at 550°C for 100 minutes and then is cold drawn for a 90% reduction, a high critical current density (Jc) is uniformly obtained in large external magnetic fields (H). Furthermore, the Ic value is greater than that of the Nb-30 at % Zr-10 at % Ti alloy.

The tensile strength of the alloy as a mechanical property of test pieces Nos. 1 and 3 shown in Table I was measured. The measurements obtained show that the tensile strength of test piece No. 1 was 140 kg/mm$^2$ and test piece No. 3 was 160 Kg/mm$^2$. It can be seen that the tensile strength of the superconducting alloy wire treated by the method of the present invention is very high. (The heat treatment time during the $\alpha$ phase precipitation heat treatment was 100 minutes.) The critical current density in the external magnetic field of 70 KOe was more than $5 \times 10^4$ A/cm$^2$.

As is apparent from the above description, the method of treatment of superconducting alloys of the present invention comprises the steps of heat treating the alloy in the peritectoid range, subjecting the alloy to an $\alpha$ phase precipitation heat treatment and cold working the alloy between the heat treatments whereby an alloy of a fine and non-homogeneous structure is obtained. The method of treatment makes it possible to improve the critical current value of the alloy over a wide range from a low magnetic field of 30 KOe to a high magnetic field of 90 KOe. It has also been found that the addition of Ta to the alloy composition improves the workability. In addition the peritectoid heat treatment and the $\alpha$ phase precipitation heat treatment are conducted independently of one another which improves the peritectoid structure and workability of the alloy. Furthermore, among the many advantages of the present invention is that the peritectoid heat treatment and the $\alpha$ phase precipitation heat treatment can be performed at a temperature less than 700°C which alleviates the problem caused by the reaction of the alloy with the copper coating.

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the invention as set forth herein.

What is claimed is:

**1.** A method of working and treating Ti-Nb-Zr-Ta superconducting alloy consisting of 10–50 at % Ti, 20–50 at % Nb, 10–40 at % Zr and 5–12 at % Ta to achieve a fine and non-homogeneous structure which comprises the steps of:

forming a $\beta$ solid solution of said Ti-Nb-Zr-Ta alloy by heating the alloy to a temperature within the $\beta$ solid solution range;

cooling and cold working said heated Ti-Nb-Zr-Ta alloy;

heating said cold worked alloy to a temperature within the $(\beta'+\beta'')$ phase region and then cooling said heated $(\beta'+\beta'')$ alloy to maintain the peritectoid structure;

cold working the peritectoid alloy;

forming a multi-phase $\beta'+\beta''+\alpha$ ($\omega$) eutectoid alloy structure by heating said peritectoid alloy to a temperature within the $(\beta'+\beta'' \rightarrow \beta'+\beta''+\alpha(+\omega)$ eutectoid structure range and then cooling said eutectoid alloy; and

cold working the eutectoid alloy.

* * * * *