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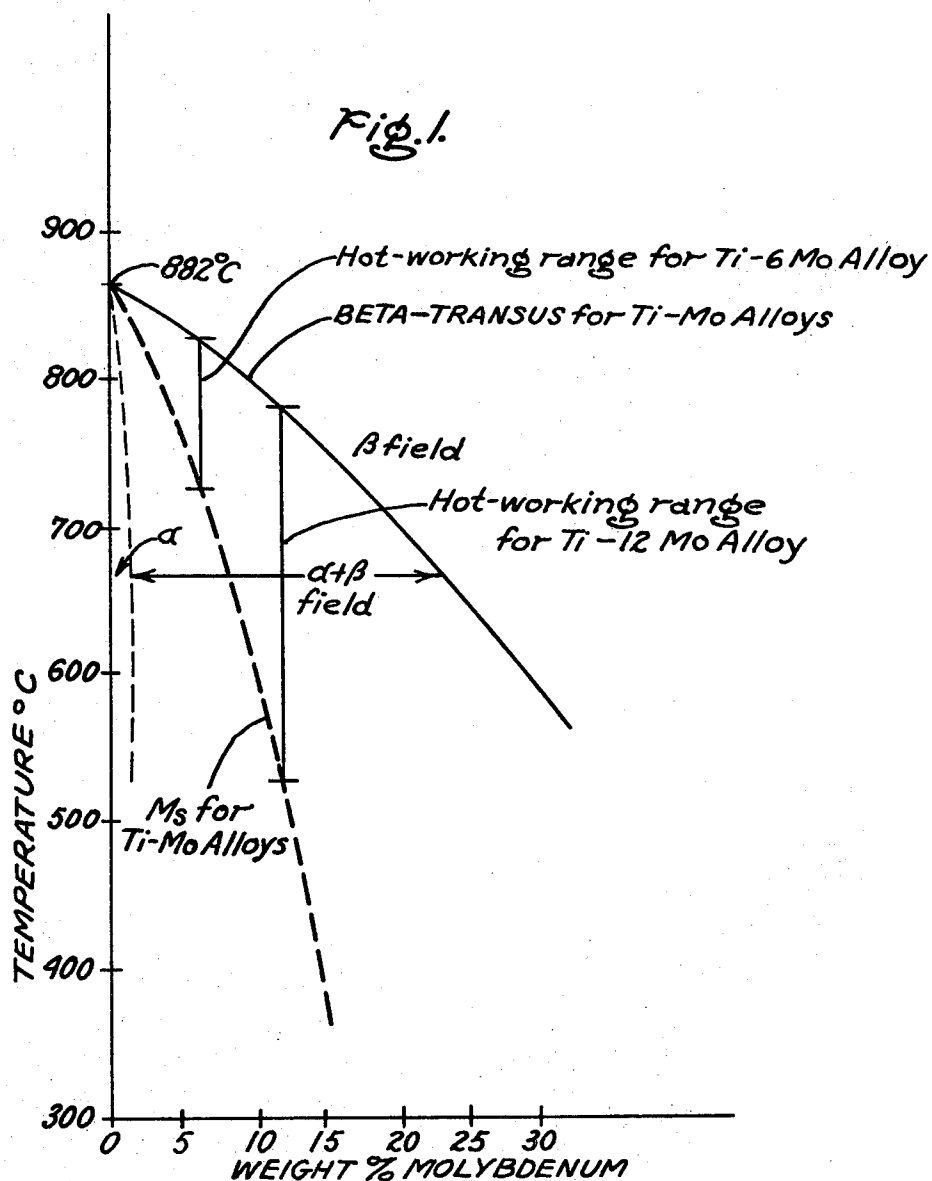
D. LEE

3,686,041

METHOD OF PRODUCING TITANIUM ALLOYS HAVING AN ULTRAFINE
GRAIN SIZE AND PRODUCT PRODUCED THEREBY

Filed Feb. 17, 1971

3 Sheets-Sheet 1



Inventor:
Daeyong Lee,
by *Am. Institute*
His Attorney.

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D. LEE

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Fig. 2.

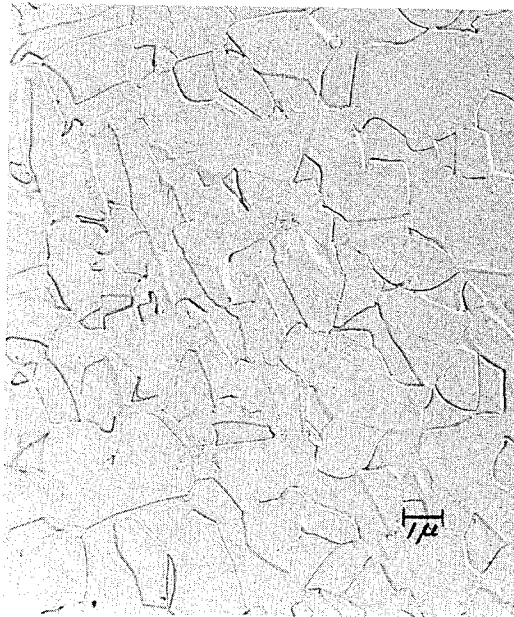
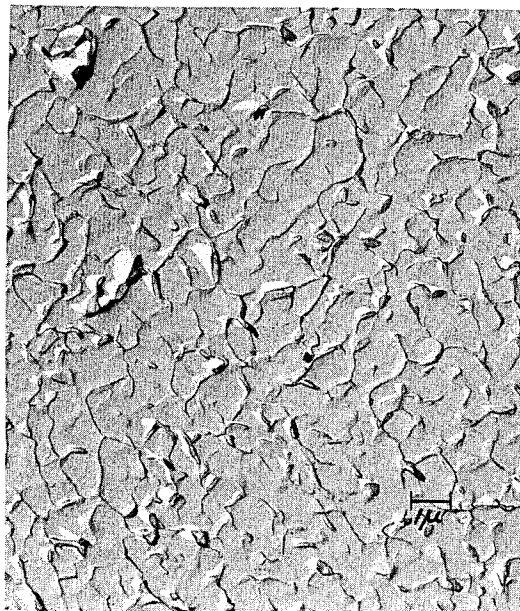


Fig. 3.



Inventor:
Daeyong Lee,
by *William H. Kristin*
His Attorney.

Aug. 22, 1972

D. LEE

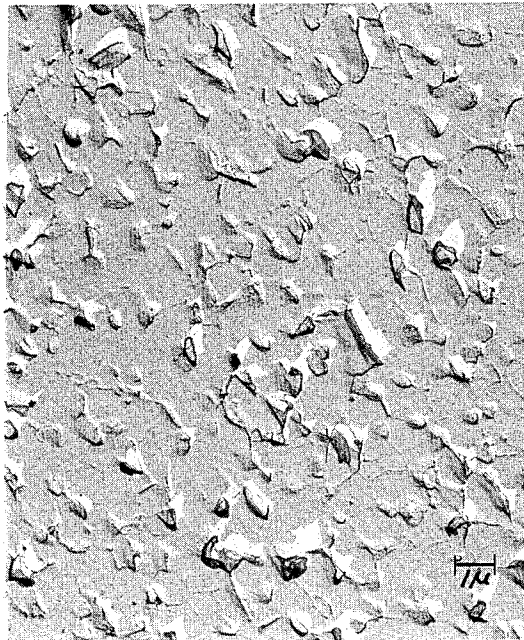
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Fig. 4.



Inventor:
Daeyong Lee,
by *[Signature]*
His Attorney.

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METHOD OF PRODUCING TITANIUM ALLOYS HAVING AN ULTRAFINE GRAIN SIZE AND PRODUCT PRODUCED THEREBY

Daeyong Lee, Scotia, N.Y., assignor to
General Electric Company

Continuation-in-part of application Ser. No. 787,838,
Dec. 30, 1968. This application Feb. 17, 1971, Ser.
No. 116,069

Int. Cl. C22f 1/18

U.S. Cl. 148—11.5 R

10 Claims

ABSTRACT OF THE DISCLOSURE

A process is disclosed for producing ultrafine grained titanium alloy microstructures which involves heating the titanium alloy body to a temperature below the alloy's beta transus temperature but above its martensitic transformation temperature, hot working the heated alloy body as its temperature decreases, quenching, and repeating the cycle at least once.

This application is a continuation-in-part of my co-pending application Ser. No. 787,838, now Patent No. 3,615,900, entitled: Process for Producing Articles With Apertures or Recesses of Small Cross Section and Product Produced Thereby, filed Dec. 30, 1968 in the name of Daeyong Lee and assigned to the same assignee as the present application.

This invention relates to titanium alloy bodies having an ultrafine grained microstructure, and to a method of producing such microstructures.

Most titanium alloys cannot readily be worked at room temperature. Working and shaping of titanium alloys for high temperature use, such as for jet engine parts, requires a fine grain size to make possible a high degree of plastic deformation (superplasticity). In order to achieve a superplastic behavior in such alloys, for good workability and formability it is desirable to have an ultrafine grain size in the alloy, namely about 1 to 5 microns. Such ultrafine grain size helps, not only for high temperature working of the alloys, but also contributes to improved mechanical properties at lower temperatures (below one-half of the melting point).

It is therefore an object of the present invention to provide a method for producing in titanium alloy bodies microstructures of ultrafine grain size.

Another object of the invention is to provide a method for hot working titanium alloys which will produce therein an average grain size of less than about 5 microns.

Another object of the invention is to provide a method for hot working a titanium alloy body at a temperature at which the alloy is in a plural phase condition in order to impart superplastic properties to the alloy.

Still another object of the invention is to provide titanium alloy bodies having a microstructure with an ultrafine grain size.

SUMMARY OF THE INVENTION

These and other objects of the invention are achieved by heating an alloy body to a temperature below the specific alloy's beta transus temperature but above its martensitic transformation temperature, hot working the heated alloy body as its temperature cools, quenching to room temperature, and repeating the cycle at least once.

According to another feature of the invention, the specific titanium alloy bodies contain, in their compositions, at least one beta-phase stabilizer, such as vanadium, molybdenum, iron, manganese or chromium. The hot working takes place while the alloy body is at a tem-

perature at which the microstructure has a plurality of phases, at least alpha-phase plus beta-phase.

Briefly stated, the process of the present invention comprises providing an alloy having the characteristic of being comprised of at least two phases in the solid state. These two phases may be alpha phase and beta phase. The alloy is treated to produce at least one phase in an ultrafine form distributed in a matrix comprised of the second or other phases.

In a preferred embodiment of the present invention, a solid titanium-base alloy which has a two-phase structure and which undergoes partial martensitic transformation is used. The martensitic phase appears within a specific temperature range during cooling. The process of treating such an alloy to produce a phase in ultra-fine grain size form comprises providing the alloy in cast or other form, plastically deforming the alloy after heating the alloy to a temperature at least above the temperature at which the martensitic transformation occurs for a time sufficient to homogenize the structure, quenching it to room temperature, re-heating the quenched solid to a temperature above the temperature at which the martensitic transformation occurs and working said hot solid to produce at least one phase in a fine form. For this type of alloy, the working of the hot solid in the two phase solid region, i.e. above the temperature at which the martensitic transformation occurs, results in at least one phase being produced in an ultra-fine grain size form. Repeated heating of the alloy to the two-phase solid region above the martensitic transformation temperature, but below the beta transus temperature and reworking of the alloy in this region will produce a distributed phase of an even finer grain size form. The alloy can be hot-worked suitably by methods such as rolling or swaging.

There are a number of alloys of certain composition which are comprised of at least two phases and which undergo partial martensitic transformation during cooling. Such alloys and their compositions are known from the literature. Representative of such alloys are Ti-Mo, Fe-C, Ti-V, Fe-Ni, Au-Cd, Fe-Ni-C.

Generally, in carrying out the instant process, the alloy components are melted together to obtain as uniform a molten sample as possible. The molten sample is then cast by a conventional method to the desired size.

The cast alloy is plastically deformed to at least partially destroy its cast structure. A number of methods are suitable for carrying out such deformation. For example, the alloy can be worked while hot and plastic by methods such as extrusion, rolling, compression or swaging. The specific temperature at which the alloy is hot worked depends largely on its malleability at such temperature, but in order to obtain the ultra-fine grain size of the desired phase structure the range of hot working temperature must be between the beta transus temperature and the martensitic temperature.

DESCRIPTION OF THE DRAWINGS

The invention will be better understood from the following description taken in conjunction with the accompanying drawings wherein:

FIG. 1 is a plot of temperature versus concentration in weight percent for molybdenum, and illustrating, as a typical example, the hot working temperature range of the present invention for titanium alloys containing, as a beta stabilizer, molybdenum;

FIG. 2 is an electron micrograph (7500X) of a titanium base alloy containing 6 wt. percent molybdenum, and illustrating the ultrafine grain size microstructure achieved by processing according to the present invention;

FIG. 3 is an electron micrograph (7500 $\times$) of a titanium base alloy containing 12 wt. percent molybdenum and processed according to the present invention;

FIG. 4 is an electron micrograph (7500 $\times$) of a titanium alloy containing 12 wt. percent molybdenum and 0.4 wt. percent silicon processed according to the present invention;

There are broadly two categories of alloys where ultrafine grain size may be obtained. In eutectic and similar alloys, the fine grain size is provided by the inherent structure itself. However, in titanium alloys, where various forms of phase transformation takes place, ultrafine grain size is not inherent in the structure itself and heretofore no simple process was known for achieving it. The present invention accomplishes this and by thermomechanical processing; that, is by a series of steps which includes hot working the alloy at a temperature below the beta-transus temperature, but above the martensitic transformation temperature, and then quenching from the hot working temperature, and repeating the heating and quenching.

All parts, proportions or amounts used herein are by weight unless otherwise noted.

The invention is further illustrated by the following examples.

Example 1

A 94% titanium-6% molybdenum alloy button (Composition A of Table I) was cast in a vacuum by means of an arc-melting. Each of the components was about 99.999 percent pure. The button was about $\frac{3}{4}$ inch thick. Two opposed periphery portions of the button were machined off to produce parallel sides. The resulting structure, i.e. workpiece, had a diameter of two inches and was about $\frac{3}{4}$ inch in height. It was wrapped in titanium foil to prevent oxidation of the titanium and heated in a furnace having an atmosphere of purified helium. All subsequent heatings of the alloy workpiece were also carried out in an atmosphere of purified helium. When the workpiece attained a temperature of 1200° C., it was removed from the furnace and forged by means of a drop hammer to a thickness of 0.385 inch to destroy its cast structure.

The workpiece was then heated in the furnace to a temperature of 800° C. and was maintained at this temperature for 30 minutes to homogenize its structure and then water quenched to room temperature.

The workpiece was then heated to a temperature of 700° C. which is above the temperature at which the martensitic transformation occurs, and hot rolled for about 20 seconds. This heating and hot rolling procedure was repeated two more times and then the workpiece was water quenched to room temperature. Its thickness by this procedure was reduced to 0.243 inch. It was then reheated to 750° C., hot rolled and water quenched to room temperature resulting in a thickness of 0.187 inch. It was then heated to 800° C., hot rolled and water quenched to room temperature resulting in a thickness of 0.138 inch.

The workpiece was then heated to 750° C. and main-

tained at this temperature for $\frac{1}{2}$ hour to stabilize its structure. It was then rapidly cooled in air to room temperature.

The temperature at which the martensite transformation from beta solid solution to the alpha prime supersaturated solid solution takes place is referred to herein as the "martensite transformation temperature" (M_s curve).

In all cases the M_s curve decreases with increasing amounts of all elements. (See The Martensite Transformation Temperature in Titanium Binary Alloys, by Pol Duwez, Trans. ASM, 45, p. 934 (1953).)

The precise location of the M_s temperature for each specific composition will depend upon several factors. Among these are the amount of impurities and state of equilibrium, both of which will vary under normal conditions. The usual impurities will be: O, N, H and C. Variations from the ideal state of equilibrium will also affect the state of microstructure, as will the prior working. The rate of quenching from above the M_s temperature will also cause a variation from equilibrium conditions and thus affects the precise location of the M_s temperature. All these factors show that the precise M_s temperature in each case is difficult to determine, but the specific temperature can be approximated closely under each set of conditions, taking the effect of the above factors into consideration.

In FIG. 1, the β -transus curve and the martensitic transformation (M_s) curve are illustrated, using titanium-molybdenum binary alloys as typical and for illustration purposes only. Above the beta-transus line, the alloy is in single phase and grain growth is very rapid, and the grain structure of alloys quenched from this beta-phase field will have extremely large grain size, e.g. 500 to 1000 μ . In the alpha-beta field, above the martensitic transformation temperature, two phases exist, alpha-phase plus beta-phase, and grain growth is more sluggish. Hot working within this temperature range breaks up and refines the grains, and quenching therefrom, and then repeating the working and quenching, produces an ultrafine grain size. Some of the beta-phase during the rapid quench in water to room temperature, is transformed into martensite, but as ultrafine grains, which improves the desirable mechanical properties.

The following further examples are given as illustrative of the method of the present invention and four typical alloys are given for the purposes of illustration, but these typical examples are not intended to limit the present invention to only these compositions.

Table I below lists the compositions of four illustrative compositions, identified as A, B, C and D. In Example 1 above, forging was one method of hot working. In the following Examples 2, 3, 4 and 5 each of the samples were processed by heating and hot-rolling in three successive steps.

TABLE I.—PROCESSING SEQUENCE OF 4 TYPICAL ALLOYS

Processing steps	Alloy compositions			
	A	B	C	D
	Ti-6Mo	Ti-12Mo	Ti-12Mo- .4Si	Ti-6Al4V
Example				
	2	3	4	5
Initial heating, ° C.	700	680	680	700
First hot working:				
Percent reduction	40	40	40	40
Reheating to—° C.	750	710	710	750
Second hot working:				
Percent reduction	20	20	20	20
Reheating to—° C.	800	740	740	800
Third hot working: Percent reduction	20	20	20	20
Final anneal (to achieve equal amounts α and β phases) (10 minutes), ° C.	812	732	732	812

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From an initial thickness of about 0.26 inch the final thickness of the specimens, after the above sequence of steps of reduction by hot rolling, was about 0.100 inch thick. Total reduction was about 62%. The range of temperatures in the above table is $\pm 25^\circ$ C. from the specific temperature shown. The actual temperatures employed should preferably be as low as possible, within the permissible range, to minimize contamination. Thus, in Example 2 above, where the nominal initial temperature shown in Table II is 700° C., this approximates the M_s temperature. The subsequent temperatures to which the body is heated for successive hot working is increased. Since M_s is difficult to determine, as mentioned above, especially for the first working step, it is better to start the treatment at the lower end of the working range, and then increase the temperature for the subsequent treatments. However, it is important that at least the final hot-working step be within the range of the martensitic transformation temperature and the beta-transus temperature.

In Examples 3 and 4, the hot working temperatures are lower than those in the other examples because the M_s temperature drops with increasing amounts of alloying additives, as shown in FIG. 1.

The Compositions A, B, C and D in Table I were selected as typical for illustrative purposes for the following reasons, in addition to the fact that good results are demonstrated. Composition C is the same as Composition B, but with about 0.4 wt. percent silicon added for strengthening the alloy by forming a dispersion within the matrix, in addition to the strengthening brought about by the ultrafine grain size achieved by the method steps of the invention.

TABLE II.—TYPICAL ROOM TEMPERATURE MECHANICAL PROPERTIES
[Three-step hot rolling, plus annealing per Table I]

Ex. No.	Material	0.2% offset yield stress, p.s.i.	Tensile strength, p.s.i.	Total elonga- tion, percent	Reduction of area, percent
2	Ti-6Mo (812° C./10 min.).	73,000	85,200	37.0	52.0
3	Ti-12Mo (732° C./10 min.).	88,000	100,500	40.6	54.9
4	Ti-12Mo-0.4Si (732° C./10 min.).	105,000	110,000	28.0	32.0

TABLE III
[Seven step cold rolling (46% reduction in thickness) plus anneal]

Ex. No.	Material	0.2% offset yield stress, p.s.i.	Tensile strength, p.s.i.	Total elonga- tion, percent	Reduction of area, percent
5	Ti-12Mo (732° C./10 min.).	109,500	115,400	13.1	48

For comparison purposes, Table III shows mechanical properties an alloy corresponding to Composition B, but instead of the hot working according to the 3-step process of Example 3, a 7-step cold rolling to 46% reduction was used. It will be observed, from a comparison of Examples 3 and 5, that the present invention results in a much higher ductility, as expressed in percent elongation and percent reduction of area.

It will be obvious to those skilled in the art upon reading the foregoing disclosure that many modifications and alterations in the method steps and in the specific compositions may be made within the general context of the invention, and that numerous modifications, alterations and additions may be made thereto within the true spirit and scope of the invention as set forth in the appended claims.

What is claimed is:

1. A process for producing ultrafine-grained alloy microstructures which comprises the steps of:

(a) subjecting an alloy body to at least two cycles of heating and hot-working which include

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(b) heating said body to a temperature below the alloy's beta-transus temperature but above its martensitic transformation temperature,

(c) said hot-working of the heated alloy body being performed as its temperature decreases, and

(d) quenching the hot-worked body.

2. A process according to claim 1, said alloy body consisting essentially of a titanium-base alloy.

3. A process according to claim 2, said titanium alloy having a composition containing essentially about 6 wt. pct. aluminum and about 4 wt. pct. vanadium.

4. A process according to claim 2, said titanium alloy having a composition containing essentially about 12 wt. pct. molybdenum.

5. A process according to claim 2, said titanium alloy having a composition containing essentially about 18 wt. pct. molybdenum.

6. A process according to claim 2, said titanium alloy having a composition containing essentially about 12 wt. pct. molybdenum and about 4 wt. pct. silicon.

7. A process according to claim 1, at least the last of said cycles of heating and hot-working being performed above the martensitic transformation temperature and below the beta-transus temperature.

8. A process for producing superplastic alloy bodies having an ultrafine grained microstructure, comprising the steps of plastically deforming said alloy body within a temperature range above the temperature at which martensitic transformation occurs but below its beta-transus temperature, quenching said alloy body, re-heating said alloy to said temperature range and again plastically deforming said body to produce at least one phase in ultrafine grain size form, and quenching said alloy body.

9. A process according to claim 7, said plastic deforma-

tion being sufficient to cause at least 20% reduction at each plastic deformation.

10. A process according to claim 8, said plastic deformation comprising uniform reduction in thickness throughout said body.

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L. DEWAYNE RUTTEDGE, Primary Examiner

W. W. STALLARD, Assistant Examiner

U.S. Cl. X.R.

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