

Title**An Alloying System****Technical Field**

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The invention concerns an alloying system for preparing a titanium alloy. In particular, the invention concerns an alloying system for preparing a titanium alloy for cold forging.

10 **Background of the Invention**

Titanium (Ti) alloys are found in a variety of structural applications. Existing Ti alloys use a wide range of alloying elements to provide certain desired characteristics such as increased tensile strength and ductility. Generally, Ti alloys exist in one or a mixture of two basic crystalline structures: the alpha phase which is a hexagonal close packed (HCP) structure, and the beta phase which is a body-centered cubic (BCC) structure. Pure titanium undergoes allotropic transformation from the alpha (α) to beta phase (β) at about 882°C. Elements which promote higher transformation temperatures are known as alpha stabilizers. These include aluminium and lanthanum. Elements which promote lower transformation temperatures are known as beta stabilizers. Beta stabilizers are classified into two groups: isomorphous beta stabilizers such as zirconium, molybdenum, niobium and vanadium; and eutectoid beta stabilizers such as iron, cobalt, chromium and nickel. One popular high strength Ti alloy contains vanadium as a beta stabilizer and aluminium as an alpha stabilizer (Ti-6Al-4V). This Ti alloy is used in the aircraft industry and medical implants.

To improve the strength of Ti, alloying additions such as aluminium, vanadium, zirconium, molybdenum are added to the Ti base material. Alloying additions reduce or elevate the allotropic transformation temperature of the alpha or beta phases of Ti, or contribute to increase its density. Hence, alloying additions are added in limited quantities to avoid undesired results. For example, aluminium is added to reduce the density and at the same time provide improved ductility while vanadium is added as an isomorphous beta stabilizer. However, aluminium stabilizes the alpha phase at room temperature. Additions greater than 5 wt% in aluminium results in formation of intermetallics in the alloy which limits its

processability. Excessive additions of vanadium increases the density of the alloy and thereby increases its weight.

5 Generally, the Ti alloy is heated to 900°C, above its beta transformation temperature (882.5°C) where the crystal structure changes from a HCP structure with three active slip systems to a BCC structure with forty-eight active slip systems. Forging is carried out by heating the billet to about 900°C and transferring the billet to the die which is kept at a lower temperature and the material is forged to the desired shape. Another method is isothermal forging of the Ti alloy where
10 the billet and the die are heated together to about 900°C.

Specifically, titanium alloys are highly suitable for biomedical implants because:

- they are biocompatible;
- they have a high strength to weight ratio;
- 15 • they are about five times as stiff as cortical bone (steel or cobalt chrome is ten times);
- they are light and more dense than steel or cobalt chrome;
- they have a Young's modulus of about 110 GPa compared with stainless (220GPa), and cortical bone is about 18-20GPa; and
- 20 • titanium sintered beads or fibres make excellent substrates for bone ingrowth and ongrowth.

Processing Ti alloys incur significant costs as special tools and environmental chambers to deal with temperatures in excess of 900°C are required. There is a
25 desire to process Ti alloys cost-effectively and to develop new Ti alloys previously not conceived.

Summary of the Invention

30 In a first preferred aspect, there is provided an alloying system for preparing a titanium alloy, the system comprising:

a rotating mill to mechanically alloy a mixture of elemental powders in predetermined proportions, the elemental powders including titanium particles, alpha stabilizer particles and beta stabilizer particles;

35 wherein the mixture is mechanically alloyed using low impact energy to layer the titanium particles with beta stabilizer particles whereby sintering of the

mechanically alloyed mixture produces alternate layers of alpha and beta stabilizer particles.

The mixture of elemental powders may be mechanically alloyed in an inert gas atmosphere.

The typical impact energy rate of a tumbler mill may be in the range of 0 to 1 Joules/hit and the impact rate is of similar magnitude to the rotational speed. In contrast, high energy planetary mills have impact energy reaching 200 Joules/hit depending on the rotational speed, and the impact rate is significantly higher than the magnitude of rotational speed. The table below gives the typical kinetic energy of impact of various mills used in a mechanical alloying process:

	Vibratory mills			Planetary ball mills			Horizontal mills
	Attritor [27]	Pulv. O [27]	SPEX [27]	Pulv. P5 [27]	G7 [18, 19]	G5 [18, 19]	MHRM (this work)
Velocity of the ball (m/s)	0-0.8	0.14-0.24	<3.0	2.5-4	0.24-6.58	0.28-11.24	0-1.247
Kinetic energy (10^{-3} J/hit)	<10	3-30	<120	10-400	0.4-303.2	0.53-884	0-190
Shock frequency (Hz)	>1000	15-50	200	~100	5.0-92.4 (5 balls)	4.5-90.7 (5 balls)	0-2.4 (1 rod)
Power (W/g ball or rod)	<0.001	0.005-0.14	<0.24	0.01-0.8	0-0.56	0-1.604	0-0.1

Tumbler mill impact energy depends on the diameter of the drum used and the speed. In one embodiment of the present invention, a 100 mm diameter drum with a speed of 65 revolutions per minute is used

The rotating mill may be a tumbler mill. The tumbler mill may have a charge to ball ratio of 1:2 in volume or higher depending on the type of phase distribution desired. The tumbler mill may use Al_2O_3 balls. The balls may have a diameter of 5, 10 and 20mm and are in the ratio of 40:40:20 of all the balls, respectively. The speed of the tumbler mill may be 65 to 70 revolutions per minute.

The tumbler mill may asynchronously rotate the centre points of the top and bottom of the drum in an ellipsoidal orbit so that the charge and the balls are forced to move within the drum where the balls impact on a new surface for every rotation.

The path of the drum may be a helix to ensure uniformity. This minimizes the temperature rise due to impact as the impacts at the same location are not successive thus producing the required distribution of phases. In one example, a laboratory scale model may be used with a 100 mm diameter x 180 mm cylindrical can with the ends closed used as mixing drum.

Preferably, the beta stabilizer particles include an amount of 1 to 5% by weight of zirconium as an isomorphous stabilizer.

Preferably, the beta stabilizer particles include an amount of 1 to 2% by weight of iron as an eutectoid stabilizer.

Preferably, the alpha stabilizer particles include an amount of 2 to 4% by weight of aluminium.

Preferably, the inert gas atmosphere is argon.

The titanium alloy produced by the present invention has 650 to 800 MPa ultimate tensile strength (UTS). The titanium alloy has an elastic modulus in the range of 40 to 45 GPa. After forging, the elastic modulus of the titanium alloy is approximately 40 GPa.

In a second aspect, there is provided a method for preparing a titanium alloy, the method comprising:

mechanically alloying a mixture of elemental powders in predetermined proportions, the elemental powders including titanium particles, alpha stabilizer particles and beta stabilizer particles;

wherein the mixture is mechanically alloyed using low impact energy to layer the titanium particles with beta stabilizer particles whereby sintering of the mechanically alloyed mixture produces alternate layers of alpha and beta stabilizer particles.

Advantageously, the mechanically alloyed mixture enables forging of the titanium alloy below its recovery temperature. Generally, the recovery temperature is less than 380°C. Preferably, the titanium alloy is forged at a temperature between 200°C to 400°C depending on the complexity of the part to be forged and the preform design.

The mixture of elemental powders may be mechanically alloyed in an inert gas atmosphere.

The method may further comprise the step of sieving the mechanically alloyed mixture. A 325-mesh sieve may be used to remove the balls and contaminants from the mechanically alloyed mixture.

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The method may further comprise the step of compacting the mechanically alloyed mixture into a preform. The mixture may be compacted to tensile bars and 10mm die pellets.

10 The method may further comprise the step of sintering the preform to consolidate the mechanically alloyed mixture. The preform may be sintered at a temperature ranging from 1110°C to 1300°C. The preform may be sintered for one to two hours. Sintering may occur in an inert gas atmosphere such as argon.

15 A forging die may be prepared for the preform. The method may further comprise the step of positioning the preform in the forging die.

The method may further comprise the step of isothermally forging the sintered preform into a predetermined shape such as a hip stem.

20 The method may further comprise the step of isothermally heating tooling and the preform to 200°C to 500°C.

Preferably, the sintered preform is isothermally forged at a temperature ranging from 200°C to 350°C at a stress rate ranging from 0.5 to 1 bar/second (18 to 37 Kg/second). The sintered preform may be forged at stress rates ranging from 0.1 to

25 10 MPa/second.

The sintered preform may be forged using a lubricant. The lubricant may be graphite or molybdenum disulphide.

30 Advantageously, cold forging of titanium alloys provides a better surface finish, lower processing costs, reduces expensive tooling costs, improves dimensional accuracy and achieves net shape forging.

35 In a third aspect, there is provided a titanium-base alloy consisting essentially of the following alloying components:

an amount from about 1 to about 5% by weight of zirconium;

an amount from about 1 to about 2% by weight of iron; and

an amount from about 2 to about 4% by weight of aluminium.

Brief Description of the Drawings

- 5 An example of the invention will now be described with reference to the accompanying drawings, in which:
- Figure 1A is a pictorial representation of a tumbler mill showing the movement of powder;
- Figure 1B is a pictorial representation of the rotation of the drum top and bottom
10 centres along an ellipsoidal orbit;
- Figure 2 is a process flow diagram of preparing a titanium alloy;
- Figure 3 is a table of compositions for titanium alloys and an XRD spectrum of a specific composition;
- Figure 4 is an XRD spectrum of a specific composition mechanically alloyed for
15 forty hours and sintered in argon for two hours at 1250°C, and an illustration of the microstructure;
- Figure 5 is a graph of the average room temperature and elevated temperature tensile strength and strain of the compositions; and
- Figure 6 is a STA thermogram of two compositions showing the variation in DTA
20 spectrum due to phase transitions.

Detailed Description of the Drawings

- Referring to Figures 1A and 1B, there is provided an alloying system 10 for
25 preparing a titanium alloy and forging of the titanium alloy at temperatures as low as 200°C to 400°C. The system comprises a tumbler mill 20. The tumbler mill 20 mechanically alloys a mixture 22 of elemental powders in, preferably, an inert gas atmosphere such as argon. The elemental powders 22 are weighed in predetermined proportions. The elemental powders 22 include titanium particles,
30 alpha stabilizer particles (aluminium) and beta stabilizer particles (iron and zirconium). The mixture 22 is mechanically alloyed using low impact energy provided by the tumbler mill 20 to layer the titanium particles with beta stabilizer particles. Turning to Figure 1B, a series of shots illustrates that the tumbler mill 20 asynchronously rotates the centre points of the top and bottom of the drum in an
35 ellipsoidal orbit. This is so that the charge 22 and the balls 21 are forced to move within the drum where the balls 21 impact on a new surface for every rotation. The path of the drum is a helix to ensure uniformity. This minimizes the temperature

rise due to impact as the impacts at the same location are not successive thus producing the required distribution of phases. During sintering of the mechanically alloyed mixture, alternate layers of alpha and beta stabilizer particles are produced.

5 Referring to Figure 2, the powders 22 are weighed 30 in their respective proportions of (1-3) wt% Al, (1-3) wt % Fe and (1-5) wt% Zr and Ti, the balance. The alloying additions of Fe and Zr is kept lower mainly due to their effect on the creep resistance and oxidation resistance respectively. Fe has a higher interdiffusion coefficient in Ti and has a retained beta phase on cooling. Alloying of
10 Fe contributes to an increase in the proof strength of the alloy but decreases the cryogenic toughness of the Ti alloy. The powders 22 are filled in a plastic container 23 together with Al_2O_3 milling balls 21 with a charge to ball ratio of 1:2 (volume). The balls 21 have a diameter of 5, 10, and 20 mm in the ratio of 40:40:20%, respectively, of the total number of balls 21. The tumbling speed in the tumbler
15 mixer 20 is set to 65 to 70 revolutions per minute. The powders 22 are alloyed 31 in the tumbler mixer 20 for a time period varying from eight to forty-eight hours. This allows an optimum combination of the phases in the blend 22 to be obtained. That is, to have alpha phase particles coated with a thin layer of beta phase particles.

20 The tumbler mill 20 does not cause wear particles from the balls 21 to contaminate the blend 22 as this results in inferior properties of the alloy blend. One reason is that the tumbler mill 20 uses low impact energy. The tumbler mixer 20 exposes a new surface of each titanium particle for every cycle of tumbling. This increases the
25 uniformity of the phase distribution. Tumbler milling has very low impact energy to produce alloying. The tumbler mill 20 produces a thin surface coating of beta phase on the Ti particles. During sintering, alternate layers of alpha and beta phases are created. The beta phase appears predominantly as a grain boundary phase to help in deformation while the alpha phase is relatively unaffected.

30 After mechanical alloying, the plastic containers 23 are carefully opened to avoid any oxidation of the powders 22. The contents of the plastic containers 23 are sieved 32 to remove the balls 21 and any contaminants, and to collect the mechanically alloyed powder blend 22. The alloyed powders 22 are sieved using a
35 325-mesh sieve (not shown). The alloyed powders 22 are removed and subjected to XRD analysis and SEM analysis for phase formation and morphological studies.

Next, the powders 22 are placed 33 in a preform (not shown) and compacted 34 to tensile specimens. The mechanically alloyed powders 22 are compacted using a fabricated preform die (not shown) at compaction pressures ranging from 400 to 600 Mpa (~25 tons of force) The alloyed powders 22 are compacted in to tensile specimens and 10mm die pellets (not shown).

The compacted mechanically alloyed powders are sintered 35 in argon at 1250°C for two hours. Alternatively, they can be sintered in a vacuum. The hardness of the preform is maintained at 280 to 370 Hv depending on the composition used. Figure 3 provides a table of the compositions tested. During sintering, the ratio of the phases is altered to provide greater uniform distribution. The beta phase is identifiable by whitish grains while the alpha phase is seen as dull grayish grains. These are both qualitatively identified by comparison with standard microstructures as well as spot EDX analysis to see the local composition of the grains. Both the alpha and beta phases were substantially uniformly distributed on the surface. The intermetallics that formed are seen as dark gray globules on the grains. Referring to Figure 5, strength increases upon increasing the temperature while the strain also increases. The increase in strength is in conformity with the STA observation and the phase changes observed with XRD. Referring to Figures 3 and 4, the XRD spectrum of composition 6 after mechanically alloying is shown, and the microstructure of composition 6 is shown.

A preform (not shown) is designed with the basic shape of a hip stem in order to position the sintered preform in a forging die (not shown). The forging die is designed based on the final shape required and is fabricated. The die and the heating assembly are housed in a die shoe (not shown) to be placed between a ram and bottom platen. The die wall surface is lubricated 36 with a coat of molybdenum disulphide and allowed to dry during heating. Alternatively, graphite can also be used as a lubricant for forging. Graphite produces a smooth surface but is not a very effective lubricant. Advantageously, MoS_2 produces defect free forging. The forging die is isothermally heated 37 using a strip heater (not shown) to a temperature ranging between 200°C to 500°C.

The preform is then placed 38 over the hot die cavity and positioned to avoid non-uniform distribution of forces during forging. Forging 39 is carried out at stress rates varying from 0.5 to 10 bar/second (0.05 to 1MPa/second) at different temperatures from 200°C to 350°C in steps of 30°C. Forging 39 at 200°C and

230°C requires very low stress rates. The stress rates are used in this to obtain control of strain rates during forming for the forging to be successful without any defects. In contrast, samples forged at temperatures greater than 250°C require moderate strain rates to obtain forging.

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The microstructure of the cross section of the forging near the base of the hip stem where beta phase grains (whitish grains) are elongated while the alpha phase maintains the original shape and size. Near the neck in the forging, the grains are relatively underformed where grain boundary sliding possibly dominates the deformation. While close to the case where the cross sectional area reduces resulting in an increase in local stress beta phase grains elongates to accommodate the plastic flow in the materials. This illustrates that the beta phase plays an active role in deformation compared to the alpha phase. Thus, this eliminates the need for very high temperatures for forging.

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Thermal Analysis

Referring to Figure 6, the compositions are mechanically alloyed for forty hours and sintered in argon for two hours. The compositions are tested for phase transformations (25°C) to 800°C using a scanning temperature analyzer (not shown). Figure 6 depicts the STA thermogram of composition 1 and composition 6 and shows the variation in DTA spectrum due to phase transitions.

The thermogram shows that the alpha to beta transformation initiates at approximately 400°C. This is indicated by a change in slope of the DTA curve while for the rest of the compositions the transformation is possibly gradual from 100°C onwards indicated by the changing slope of the DTA curve. All the compositions show an increase in strength up to 100°C with higher strain during failure. The thermogram also indicates an increase in the μV until 100°C followed by a decrease in the μV values due possibly to the precipitation of intermetallics due to the reaction of individual elements with the base matrix and surrounding elements. But a further increase in temperature results in the elements aiding stabilization of beta phase by dissolving back in the matrix. Besides compositions 1 and 2, the other compositions had a negative voltage due to the stabilization of beta phase and the presence of intermetallic compounds. In order to plot the behavior on a log scale the negative values of μV are converted in to positive values. At the point of complete transformation, the μV reduces to its minimum value, negative in most compositions, indicating the transformation to beta phase. Since the log scale for

negative values cannot be plotted, the negative values have been converted into positive values with suitable adjustment to reflect the trends. Composition 6 has all the values recorded on the negative scale. This has been converted to positive numbers to reflect on the log scale. The deformation or forging of the samples are
 5 able to be conducted at temperatures of 200°C and above based on the observations of the thermogram.

Although the present invention has been described with reference to the alloying components of aluminium, iron and zirconium, the table below lists other alloying
 10 additions to Ti and their properties:

<u>Alloying Element</u>	<u>Phase Stabilized</u>	<u>Type of stabilizer</u>
Aluminium	Alpha	-
Tin	Alpha	-
Vanadium	Beta	Isomorphous (BCC)
Molybdenum	Beta	Isomorphous
Iron	Beta	Eutectoid
Niobium	Beta	Isomorphous
Tantalum	Beta	Isomorphous
Silicon	Beta	Eutectoid
Chromium	Beta	Eutectoid
Zirconium	Beta/Alpha	Isomorphous
Palladium	Beta	Eutectoid
Cobalt	Beta	Eutectoid
Manganese	Beta	Eutectoid
Hafnium	Beta/Alpha	Isomorphous

It is envisaged that Ti alloys made in accordance with the present invention are used in biomedical implants, mobile phone covers, watch casings, aerospace and automotive structural components. Other applications include precision fasteners,
 15 Ti diaphragms for microphones, Ti fingers for wave soldering machines, chassis for hard disk, cameras or notebook computers.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments
 20 without departing from the scope or spirit of the invention as broadly described.

The present embodiments are, therefore, to be considered in all respects illustrative and not restrictive.

WE CLAIM:

1. An alloying system for preparing a titanium alloy, the system comprising:
a rotating mill to mechanically alloy a mixture of elemental powders in
5 predetermined proportions, the elemental powders including titanium particles,
alpha stabilizer particles and beta stabilizer particles;
wherein the mixture is mechanically alloyed using low impact energy to
layer the titanium particles with beta stabilizer particles whereby sintering of the
mechanically alloyed mixture produces alternate layers of alpha and beta stabilizer
10 particles.
2. The system according to claim 1, wherein the rotating mill is a tumbler mill.
3. The system according to claim 2, wherein the tumbler mill has a charge to
15 ball ratio of 1:2 in volume.
4. The system according to claim 2, wherein the tumbler mill uses Al_2O_3 balls.
5. The system according to claim 4, wherein the balls have a diameter of 5,
20 10 and 20mm and are in the ratio of 40:40:20, respectively.
6. The system according to claim 2, wherein the speed of the tumbler mill is
65 to 70 revolutions per minute.
- 25 7. The system according to claim 1, wherein the beta stabilizer particles
include an amount of 1 to 5% by weight of zirconium as an isomorphous stabilizer.
8. The system according to claim 1, wherein the beta stabilizer particles
include an amount of 1 to 2% by weight of iron as an eutectoid stabilizer.
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9. The system according to claim 1, wherein the alpha stabilizer particles
include an amount of 2 to 4% by weight of aluminium.
10. The system according to claim 1, wherein the mixture of elemental
35 powders is mechanically alloyed in an inert gas atmosphere.

11. The system according to claim 1, wherein the impact energy rate of the rotating mill is in the range of 0 to 1 Joules/hit.

12. The system according to claim 1, wherein the impact rate of the rotating mill is of a substantially equal magnitude to the rotational speed of the rotating mill.

13. The system according to claim 2, wherein the tumbler mill has a 100 mm diameter drum.

14. The system according to claim 13, wherein the path of the drum is a helix to ensure uniformity.

15. The system according to claim 13, wherein the centre points of the top and bottom of the drum are rotated asynchronously in an ellipsoidal orbit to force the powders and balls to move within the drum such that the balls impact on a new surface for every rotation.

16. The system according to claim 10, wherein the inert gas atmosphere is argon.

17. A method for preparing a titanium alloy, the method comprising:
mechanically alloying a mixture of elemental powders in predetermined proportions, the elemental powders including titanium particles, alpha stabilizer particles and beta stabilizer particles;

wherein the mixture is mechanically alloyed using low impact energy to layer the titanium particles with beta stabilizer particles whereby sintering of the mechanically alloyed mixture produces alternate layers of alpha and beta stabilizer particles.

18. The method according to claim 17, further comprising the step of sieving the mechanically alloyed mixture.

19. The method according to claim 18, wherein a 325 mesh sieve is used to remove the balls and contaminants from the mechanically alloyed mixture.

20. The method according to claim 17, further comprising the step of compacting the mechanically alloyed mixture into a preform.

21. The method according to claim 20, wherein the mixture is compacted to tensile bars and 10mm die pellets.

5 22. The method according to claim 20, further comprising the step of sintering the preform to consolidate the mechanically alloyed mixture.

23. The method according to claim 22, wherein the preform is sintered at a temperature ranging from 1110°C to 1300°C.

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24. The method according to claim 22, wherein the preform is sintered for one to two hours

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25. The method according to claim 24, wherein sintering occurs in an inert gas atmosphere.

26. The method according to claim 22, further comprising the step of isothermally forging the sintered preform into a predetermined shape.

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27. The method according to claim 26, wherein the sintered preform is isothermally forged at a temperature ranging from 200°C to 350°C.

28. The method according to claim 26, wherein the sintered preform is forged at a stress rate ranging from 0.5 to 1 bar/second.

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29. The method according to claim 26, wherein the sintered preform is forged using a lubricant.

30. The method according to claim 29, wherein the lubricant is graphite or molybdenum disulphide.

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31. The method according to claim 17, wherein the beta stabilizer particles include an amount of 1 to 5% by weight of zirconium as an isomorphous stabilizer.

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32. The method according to claim 17, wherein the beta stabilizer particles include an amount of 1 to 2% by weight of iron as an eutectoid stabilizer.

33. The method according to claim 17, wherein the alpha stabilizer particles include an amount of 2 to 4% by weight of aluminium.

34. A titanium-base alloy prepared according to the method of claim 17, the
5 alloy consisting essentially of the following alloying components:

an amount from about 1 to about 5% by weight of zirconium;

an amount from about 1 to about 2% by weight of iron; and

an amount from about 2 to about 4% by weight of aluminium.

Abstract of the Disclosure

AN ALLOYING SYSTEM

An alloying system for preparing a titanium alloy, the system comprising a rotating mill to mechanically alloy a mixture of elemental powders in predetermined proportions, the elemental powders including titanium particles, alpha stabilizer particles and beta stabilizer particles; wherein the mixture is mechanically alloyed using low impact energy to layer the titanium particles with beta stabilizer particles whereby sintering of the mechanically alloyed mixture produces alternate layers of alpha and beta stabilizer particles.

Fig. 2