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## TITANIUM BASE ALLOYS

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The present invention relates to titanium alloys and a method of making same. It more particularly relates to an improved method of making alloys in which titanium is alloyed with intermetallic compounds of titanium.

Titanium alloys are unexcelled in strength to weight ratio up to approximately 800 degrees F. Above this temperature, the strength properties of titanium alloys decrease rapidly thus limiting their usefulness.

In the method of the present invention, intermetallic compounds, such as $Ti_5Si_3$, $TiB_2$, TiC, and TiAl, are dispersed in titanium to provide an alloy that has improved strength properties at high temperature. Intermetallic compounds are ground to a fine powder and then blended with titanium hydride in a ball milling operation. Consolidation is then accomplished by vacuum hot pressing, by cold compaction and extrusion, or by cold compaction, sintering and extrusion.

It is, therefore, a general object of the present invention to provide titanium alloys having suitable mechanical properties for application at temperatures between 800 and 1200 degrees F.

Another object of the present invention is to provide sintered titanium alloys that have good properties of strength and hardness.

Still another object of the present invention is to provide an improved method of making titanium alloys by combining finely divided intermetallic compounds with titanium hydride.

Other objects and advantages of the present invention will be apparent as the same becomes better understood by reference to the following detailed description.

In the present method of making titanium alloys, very fine titanium powder (one to three microns) is needed in order to make satisfactory dispersions. As ordinary comminution techniques cause oxygen embrittlement, a special technique using titanium hydride is employed. Titanium hydride is produced by reacting grade A–1 titanium sponge with high purity hydrogen at an elevated temperature. While hydrogen is known to embrittle titanium the hydrogen can be removed by vacuum treatment at elevated temperature. The hydride sponge is ball milled inside a helium atmosphere chamber having a dew point ranging between −20 and −50 degrees F. The average size of the milled particles is about 2.5 microns and this is used as the base material.

The intermetallic compounds $Ti_5Si_3$, $TiB_2$, TiC, and TiAl have been successfully alloyed with titanium to increase its mechanical properties. These intermetallic compounds have a particle size, in the as-received condition, which is too large for use in dispersion strengthening. Consequently, it is necessary to grind these powders to as fine a particle size as possible. One method of accomplishing this is by long time ball milling in methanol in a porcelain mill using hardened steel balls as the grinding medium. As the milling time is usually about 300

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hours, the wear on the balls is quite high and it may be necessary to remove the iron from the powder. This can be accomplished by leaching the ground powder in 1:1 HCl until the filtrate shows no color with potassium cyanide (KCN). The leaching operation normally takes about 24 hours. After the leaching operation, the powder is washed with methanol and air dried.

Blending of the titanium hydride and the intermetallic compounds is also accomplished by a ball milling operation. The product of this operation is then put in a retort for vacuum outgassing treatment at 1100 degrees F. for approximately 16 hours. Consolidation can be accomplished by vacuum hot pressing, by cold compaction and extrusion, or by cold compaction, sintering and extrusion. All milling of the powder and loading of the dies is done in a chamber containing an inert atmosphere and the dies are transferred to the furnace in a protective bag.

### EXAMPLE I

Titanium hydride is ball milled for approximately 16 hours to reduce the average particle size to 1–3 microns in size. Tapping the ball mill during rotation prevents the hydride powder from packing 7 percent by volume of the intermetallic compound TiAl is added to the titanium hydride and the mixture is ball milled for approximately 8 hours. The product is then consolidated by cold compaction. The formed billets are next extruded at 1800 degrees F. to the desired shape and annealed 2 hours at 1300 F. in a vacuum. The hardness of the alloy at various temperatures is shown in Table I. This table gives hardness values for the product as extruded, and also after annealing for 18 hours at 1300 degrees F.

### EXAMPLE II

Same as Example I except that 6.3 percent by volume of the intermetallic compound $Ti_5Si_3$ is alloyed with the titanium instead of the intermetallic compound TiAl. The particle size of the $Ti_5Si_3$ is approximately 0.8 micron before mixing with the titanium. Table II lists the hardness of the alloy for three conditions, namely: as extruded and annealed 2 hours at 1300 F.; after annealing for 4 hours at a temperature of 1380 degrees F.; and after annealing for 4 hours at a temperature of 1560 degrees F. Table III lists the tensile properties of the alloy at various temperatures.

### EXAMPLE III

Same as Example I except that 5.5 percent by volume of the intermetallic compound TiC is alloyed with the titanium instead of the intermetallic compound TiAl. Table IV lists the value for hot hardness of the alloy at various temperatures. This table gives the value for hot hardness in the as extruded and annealed condition and also for an alloy that has been compacted, sintered, and extruded. Table V lists the value for hot hardness of an alloy having 5.5 percent by volume of TiC of which the average particle size is approximately 0.6 micron. Table VI lists the tensile properties of the alloy at various temperatures. Table VII shows the results of stress-rupture tests at various temperatures.

### EXAMPLE IV

Same as Example I except that 6.2 percent by volume of the intermetallic compound $TiB_2$ is alloyed with the titanium instead of the intermetallic compound TiAl. The particle size of the $TiB_2$ is approximately 0.6 micron before mixing with the titanium. Table VIII shows the hot hardness of the alloy at various temperatures, and for two conditions, namely: in the as-extruded and annealed condition, and after annealing for 4 hours at a temperature of 1560 degrees F.

*Table I*

HOT HARDNESS

[7.0 percent by v. of TiAl]

| Cold compacted, extruded and annealed 2 hours at 1,300° F. | | Cold compacted, extruded and annealed 18 hours at 1,300° F. | |
|---|---|---|---|
| Temp. ° F. | DPH | Temp. ° F. | DPH |
| RT | 478 | RT | 356 |
| 594 | 184 | 786 | 156 |
| 782 | 117 | 897 | 133 |
| 898 | 76 | 990 | 105 |
| 968 | 69 | 1,089 | 73 |
| 1,180 | 31 | 1,188 | 42 |
| 1,338 | 13 | 1,385 | 25 |

*Table II*

HOT HARDNESS

[6.3 percent by v. of $Ti_5Si_3$]

| Cold compacted, extruded and annealed 2 hours at 1,300° F. | | Cold compacted, extruded and annealed 4 hours at 1,560° F. | | Cold compacted, extruded and annealed 4 hours at 1,380° F. | |
|---|---|---|---|---|---|
| Temp. ° F. | DPH | Temp. ° F. | DPH | Temp. ° F. | DPH |
| RT | 370 | RT | 412 | RT | 258 |
| 620 | 168 | 663 | 155 | 594 | 163 |
| 812 | 149 | 821 | 127 | 778 | 114 |
| 905 | 134 | 926 | 110 | 880 | 95 |
| 1,015 | 87 | 1,006 | 91 | 981 | 82 |
| 1,214 | 36 | 1,214 | 42 | 1,180 | 38 |
| 1,402 | 18 | 1,408 | 20 | 1,391 | 19 |

*Table III*

TENSILE PROPERTIES

[6.3 percent by v. of $Ti_5Si_3$. Cold compacted, extruded and annealed 2 hours at 1,300 F.]

| Temp. ° F. | Tensile strength (p.s.i.) | Elongation (percent) | Reduction in area (percent) |
|---|---|---|---|
| 800 | 69,400 | 3.5 | 17.2 |
| 1,000 | 59,800 | 11.2 | 11.4 |
| 1,200 | 46,200 | 8.0 | 4.0 |

*Table IV*

HOT HARDNESS

[5.5 percent by v. of TiC (5 microns)]

| Cold compacted, extruded and annealed 2 hours at 1,300 ° F. | | Cold compacted, sintered, extruded and annealed 2 hours at 1,300 ° F. | | Cold compacted, extruded and annealed 18 hours at 1,300 ° F. | |
|---|---|---|---|---|---|
| Temp. ° F. | DPH | Temp. ° F. | DPH | Temp. ° F. | DPH |
| RT | 442 | RT | 435 | RT | 521 |
| 632 | 116 | 431 | 210 | 632 | 271 |
| 812 | 107 | 619 | 185 | 818 | 225 |
| 922 | 80 | 826 | 125 | 930 | 166 |
| 1,002 | 62 | 998 | 84 | 1,011 | 134 |
| 1,201 | 29 | 1,218 | 41 | 1,207 | 46 |
| 1,398 | 12 | --------- | ----- | 1,411 | 21 |



*Table V*

HOT HARDNESS

[5.5 percent by v. of TiC (0.6 micron)]

| Cold compacted, sintered, extruded and annealed 2 hours at 1,300 ° F. | |
|---|---|
| Temp. ° F. | DPH |
| RT | 415 |
| 585 | 224 |
| 778 | 192 |
| 888 | 163 |
| 977 | 131 |
| 1,175 | 63 |
| 1,380 | 25 |

*Table VI*

TENSILE PROPERTIES

[5.5 percent by v. of TiC (5μ). Cold compacted, sintered, extruded and annealed 2 hours at 1300 F.]

| Temp. ° F. | Tensile strength (p.s.i.) | Elongation (percent) | Reduction in area (percent) |
|---|---|---|---|
| RT | 142,500 | 1.17 | 0 |
| 800 | 58,600 | 9.34 | 27.8 |
| 1,000 | 43,900 | 11.6 | 37.6 |
| 1,200 | 22,600 | 31.8 | 71.0 |

*Table VII*

STRESS-RUPTURE LIFE

[5.5 percent by v. of TiC (5μ). Cold compacted, sintered, extruded and annealed 2 hours at 1300 F.]

| Temp. ° F. | Stress (p.s.i.) | Life (hours) |
|---|---|---|
| 800 | 43,000 | 2.4 |
| 800 | 38,200 | 30.9 |
| 800 | 38,000 | 7.5 |
| 800 | 33,000 | 50.5 |
| 800 | 27,800 | 118.8 |
| 1,000 | 37,300 | 0.1 |
| 1,000 | 32,900 | 0.4 |
| 1,000 | 28,500 | 0.5 |
| 1,000 | 24,100 | 2.2 |
| 1,000 | 10,000 | 292.7 |

*Table VIII*

HOT HARDNESS

[6.2 percent by v. of $TiB_2$]

| Cold compacted, extruded and annealed 2 hours at 1,300° F. | | Cold compacted, extruded and annealed 4 hours at 1,560° F. | |
|---|---|---|---|
| Temp. ° F. | DPH | Temp. ° F. | DPH |
| RT | 387 | RT | 417 |
| 585 | 245 | 645 | 199 |
| 778 | 174 | 842 | 136 |
| 884 | 143 | 913 | 113 |
| 990 | 95 | 1,020 | 76 |
| 1,190 | 29 | 1,203 | 36 |
| 1,385 | 11 | 1,393 | 16 |

Tables I, II, IV, V, and VIII show the results of Hot-Hardness tests that were carried out in a vacuum chamber containing heating elements, six sapphire 136° indenters and a rotating specimen stage. The temperature of each specimen was measured individually by a thermocouple embedded in the stage immediately beneath the specimen. The specimens were brought to temperature and held for a minimum of 15 minutes before indentations were made. Dwell time was 30 seconds. Conversion to DPH is made by measuring the impression and substituting in the formula:

$$DPH=\frac{1.854L}{d^2}$$

where:

$DPH$=diamond pyramid hardness
$L$=load in kilograms
$d$=length of diagonal in mm.

Tables III and VI show the results of tensile tests which were made using standard equipment. Elevated temperature tests were conducted by heating the specimen to the required temperature followed by a soaking period of 15 minutes. No protective atmosphere was used during the test.

Table VII shows the results of stress-rupture tests which were conducted using constant load machines. The specimens were heated to the testing temperature and allowed to soak a minimum of 15 minutes before the load was applied. No protective atmosphere was used during the test.

The mechanical properties of unalloyed titanium are shown in Tables IX, X and XI.

*Table IX*

HOT HARDNESS

[Unalloyed Titanium (2.5μ)]

| Temp. ° F.: | DPH |
|---|---|
| 77 | 259 |
| 454 | 155 |
| 818 | 90 |
| 1017 | 60 |
| 1107 | 48 |

*Table X*

TENSILE STRENGTH

[Unalloyed Ti (2.5μ TiH). Cold compacted, extruded and annealed 2 hours at 1300 F.]

| Temp. ° F. | Tensile strength (p.s.i.) | Elongation (percent) | Reduction in area (percent) |
|---|---|---|---|
| RT | 112,500 | 11.7 | 37.4 |
| 600 | 45,900 | 21.8 | 41.5 |
| 800 | 34,500 | 22.8 | 49.6 |
| 1,000 | 25,600 | 10.5 | 44.5 |
| 1,200 | 15,950 | 41.8 | 81.3 |

*Table XI*

STRESS-RUPTURE LIFE

[Unalloyed Ti (2.5μ TiH). Cold compacted, extruded and annealed 2 hours at 1300° F.]

| Temp. ° F. | Stress | Life (hours) | Elongation (percent) |
|---|---|---|---|
| 800 | 30,000 | 8.8 | 14.9 |
| 800 | 27,100 | 42.6 | 18.2 |
| 800 | 25,000 | 51.9 | 12.7 |
| 800 | 22,000 | 496.7 | 14.9 |
| 800 | 20,000 | 499.0 | 11.6 |

By comparing the data in Tables I to VIII with the data for unalloyed titanium (Tables IX to XI) it can be seen that the dispersion strengthening of titanium by the addition of intermetallic compounds is feasible. For example, at room temperature, the hot hardness of an alloy containing 7 percent of the intermetallic compound TiAl is shown to have a DPH value of 478, as compared to 259 for unalloyed titanium. By way of another example, at a temperature of 1200 degrees F., the tensile strength of an alloy containing 6.3 percent of the intermetallic compound $Ti_5Si_3$ is 46,200 p.s.i., as



compared to a tensile strength of 15,950 p.s.i. for unalloyed titanium.

It can thus be seen that the present invention discloses new and useful alloys and a method of preparing them. Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is, therefore, to be understood that the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. Sintered titanium base alloys comprised of from about 5 percent to about 7 percent, by volume, of an intermetallic compound having a grain size of from about 0.5 micron to about 5 microns, said intermetallic compound being selected from the group consisting of $Ti_5Si_3$, $TiB_2$, TiC, and TiAl, balance titanium having a grain size of from about 1 micron to about 3 microns, said intermetallic compound being dispersed in said titanium and said alloys being characterized by improved strength at high temperature and by increased hot hardness, as compared with unalloyed titanium.

2. A titanium base alloy comprised of about 6.3 percent, by volume, of the intermetallic compound $Ti_5Si_3$ having a grain size of from about 0.5 micron to about 5 microns dispersed in about 93.7 percent, by volume, of titanium having a grain size of from about 1 micron to about 3 microns, said alloy being characterized by improved strength at high temperature and by increased hot hardness, as compared with unalloyed titanium.

3. A titanium base alloy comprised of about 6.2 percent, by volume, of the intermetallic compound $TiB_2$ having a grain size of from about 0.5 micron to about 5 microns dispersed in about 93.8 percent, by volume, of titanium having a grain size of from about 1 micron to about 3 microns, said alloy being characterized by improved strength at high temperature and by increased hot hardness, as compared with unalloyed titanium.

4. A titanium base alloy comprised of about 5.5 percent, by volume, of the intermetallic compound TiC having a grain size of from about 0.5 micron to about 5 microns dispersed in about 94.5 percent, by volume, of titanium having a grain size of from about 1 micron to about 3 microns, said alloy being characterized by improved strength at high temperature and by increased hot hardness, as compared with unalloyed titanium.

5. A titanium base alloy comprised of about 7 percent, by volume, of the intermetallic compound TiAl having a grain size of from about 0.5 micron to about 5 microns dispersed in about 93 percent, by volume, of titanium having a grain size of from about 1 micron to about 3 microns, said alloy being characterized by improved strength at high temperature and by increased hot hardness, as compared with unalloyed titanium.

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