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3,756,810

HIGH TEMPERATURE TITANIUM ALLOY

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ABSTRACT OF THE DISCLOSURE

A titanium base alloy comprising 5.9 to 6.75% aluminum, 1.5 to 2.5% tin, 0.5 to 2.0% zirconium, 0.8 to 2.0% molybdenum, 0.15 to 0.6% bismuth, 0.07 to 0.18% silicon, less than 0.12% oxygen, less than 0.2% carbon and less than 0.1% nitrogen, characterized by good elevated temperature creep strength.

This invention relates to a novel titanium base alloy and more particularly to a titanium base alloy having good elevated temperature properties.

Known titanium base alloys intended for elevated temperature applications include combinations of alpha-promoting elements such as aluminum, tin and zirconium which in proper amounts, confer elevated temperature strength to the alloy by solid solution effects and/or by an ordering phenomenon. However, titanium base alloys containing only alpha-promoting elements have relatively low short time strengths at elevated temperatures and, therefore, a small amount (1 to 2%) of a beta-stabilizing element such as molybdenum is generally included in the alloy. Molybdenum strengthens the alloy without detracting appreciably from creep resistance. Additionally, silicon may be included as an alloying element in amounts up to about 0.5% to further enhance the short time strength at elevated temperatures.

While it is known to add the alpha-promoting elements to high temperature titanium base alloys, it is also known that the practical upper limits for the alpha-promoters and for silicon are relatively low and, in fact, have been reached in the known alloys. The addition of an excess of either alpha-promoting elements or silicon results in low retained ductility after creep exposure which is known as metallurgical instability and is undesirable.

Our invention is directed to a titanium base alloy with improved properties at elevated temperatures. The invention consists in adding bismuth to titanium alloys in an amount between 0.15% and 0.60% by weight to increase the short time strength and the creep strength of the alloys at temperatures up to about 1100° F. These improved properties are achieved without a significant decrease in the metallurgical stability of the alloys, and, therefore, ductility is retained after creep exposure. We have found that bismuth adds to the elevated creep characteristics of the alloy and, based test results set forth hereinafter, appears to interact synergistically with silicon and molybdenum in the alloy.

It has been determined that an alloy within the scope of our invention should have a composition within the following ranges:

Element:	Weight percent
Aluminum	5.9–6.75
Tin	1.5–2.5
Zirconium	0.5–2.0
Molybdenum	0.8–2.0
Bismuth	0.15–0.6
Silicon	0.07–0.18
Oxygen	[1] 0.12
Carbon	[1] 0.2
Nitrogen	[1] 0.1
Oxygen+Carbon+Nitrogen	[1] 0.2

Titanium	Balance

[1] Maximum.

Additionally, it has been determined that the aluminum, tin, zirconium and silicon should be present in accordance with the following relationship:

$$\text{Percent Al}+\frac{\text{percent Sn}}{3}+\frac{\text{percent Zr}}{6}+\text{percent Si}\times 4\leq 8$$

A preferred alloy having good creep resistance and good ductility after creep exposure as well as good short time strength at elevated temperatures and excellent notch tensile and notch bar impact properties has the following nominal composition:

Element:	Weight percent
Aluminum	6.25
Tin	2
Zirconium	1.5
Molybdenum	1
Bismuth	0.35
Silicon	0.1
Oxygen	[1] 0.1
Carbon	[1] 0.2
Nitrogen	[1] 0.1
Titanium	Balance

[1] Maximum.

Alloys within the scope of our invention have superior creep properties over the known elevated temperature titanium base alloys such as Ti-6Al-4V, Ti-8Al-1Mo-1V, Ti-6Al-2Sn-4Zr-2Mo, Ti-6Al-2Sn-2Zr-1Mo-1.5W-0.1Si.

A series of alloys having a base composition of Ti-6Al-2Sn-2Zr and including different amounts of bismuth, silicon and molybdenum were melted and subjected to various metallurgical tests. The actual composition and the test results for each alloy are set forth in Table I.

TABLE I[1]

Percent Mo	Percent Si	Percent Bi	Creep [2] deformation, percent	Y.S., k.s.i.	RA, percent
0.92	0	0	NE [3]	113.5	27.0
			0.535	122.0	23.5
0.91	0	0.14	NE	115.0	26.5
			0.592	126.0	26.0
0.91	0	0.24	NE	118.0	27.5
			0.497	128.5	22.5
0.91	0	0.58	NE	116.0	23.0
			0.248	125.5	17.0
0.95	0.05	0	NE	118.5	26.5
			0.375	127.0	19.0
0.93	0.06	0.13	NE	126.0	24.0
			0.453	130.5	22.0
1.00	0.05	0.25	NE	123.5	23.0
			0.187	129.5	22.5
1.00	0.05	0.89	NE	123.0	22.0
			0.071	131.5	12.5
0.97	0.11	0	NE	122.5	23.5
			0.392	130.5	20.0
1.03	0.11	0.20	NE	124.5	24.5
			0.148	127.5	24.5
1.10	0.10	0.28	NE	128.0	22.5
			0.143	129.5	16.5
1.07	0.08	0.89	NE	123.0	20.5
			0.087	128.5	9.5
1.83	0	0	NE	114.5	21.5
			0.857	125.0	17.5
1.80	0	0.19	NE	116.5	22.0
			0.601	126.5	17.0
1.86	0	0.28	NE	116.5	21.0
			0.412	126.5	15.0
1.79	0	0.89	NE	116.5	16.0
			0.318	128.0	10.0
1.90	0.05	0	NE	121.5	18.0
			0.502	129.0	14.0
1.91	0.04	0.15	NE	118.0	22.0
			0.389	129.0	15.5
2.02	0.04	0.25	NE	117.0	23.5
			0.209	128.5	19.0
1.86	0.05	1.04	NE	123.0	17.0
			0.180	128.5	8.0
1.96	0.09	0	NE	125.5	19.0
			0.426	129.0	15.0
1.97	0.10	0.14	NE	118.5	21.0
			0.181	127.5	14.5
2.07	0.09	0.22	NE	120.5	20.5
			0.180	129.0	14.5
1.93	0.09	0.70	NE	123.0	16.0
			0.156	131.5	11.5

[1] All specimens heat treated 1,950 F., 15 min., AC, plus 1,300 F. 1 hr., AC.
[2] Creep exposure 1,000 F., 45 k.s.i., 150 hrs.
[3] NE=Not creep exposed.

A consideration of Table I shows that as little as 0.15% bismuth appreciably improves the creep strength at 1000° F. and that a synergistic improvement is obtained when bismuth is included in an alloy which also includes silicon. Additionally, Table I shows that the ductility, expressed as percent RA is about 14.5% or greater for bismuth contents up to about .6%, but when excess bismuth is included in the alloy, the percent RA decreases to below 14.5% which indicates that excessive bismuth is detrimental to ductility. The table also shows that the molybdenum content of the alloy should be between 1.0% and 2.0% to provide adequate short time strength without seriously reducing creep strength or ductility.

A number of additional heats was melted and the results of metallurgical tests on these alloys are set forth in Table II.

TABLE III

Creep data [a]

Heat	Time to reach 0.2% deformation (hours)	
	1,000 F., 50 k.s.i.	1,100 F., 25 k.s.i.
V-4264	121	89
V-4263	175	137
V-4198	171	160
V-4262	238	86
V-4343	132	90
V-4300	168	101
V-4320	170	76
V-4338	75	40
V-4339	33	----------
V-4342	75	72
V-4249	81	100
V-4321	57	126
V-4292	131	230
V-4293	425	225
V-4294	245	85
V-4295	230	178
V-4296	189	125

[a] All specimens heat treated 1,950 F., 15 min., AC plus 1,300 F., 1 hr., AC.

TABLE II

Room temperature tensile and creep stability data [a]

Heat	Percent						Creep exposure	Creep def., percent	Tensile properties before and after exposure: Y.S. (k.s.i.)	Tensile properties before and after exposure: Percent RA
	Al	Sn	Zr	Mo	Bi	Si				
V-4264	5.93	2.03	2.08	1.03	0.10	0.12	None		141.0	26.0
							(1) [b]	0.177	151.0	17.5
							(2) [c]	0.153	151.0	14.5
V-4263	6.05	2.00	1.90	1.05	0.2	0.11	None		139.0	25.0
							(1)	0.097	148.5	16.0
							(2)	0.155	147.0	12.0
V-4198	5.80	1.93	1.94	1.02	0.38	0.09	None		145.0	23.5
							(1)	0.086	155.5	16.0
							(2)	0.149	151.0	14.5
V-4262	5.95	1.96	1.91	1.01	0.29	0.11	(None		136.5	23.0
							(1)	0.113	148.0	14.0
							(2)	0.218	142.5	9.5
V-4343	6.21	2.00	1.66	1.02	0.53	0.11	None		147.5	24.0
							(1)	0.116	157.0	13.5
V-4300	5.90	2.06	2.04	1.09	0.36	0.12	None		139.5	21.0
							(1)	0.113	150.5	14.0
							(2)	0.124	149.5	10.0
V-4320	6.05	2.09	1.78	1.00	0.36	0.13	None		141.0	20.5
							(1)	0.125	148.5	13.5
							(2)	0.212	152.5	9.5
V-4338	5.99	2.01	2.10	1.05	0.38	0.15	None		152.0	20.0
							(1)	0.227	163.5	13.5
							(2)	0.214	159.5	10.0
V-4339	6.01	2.04	2.09	1.07	0.37	0.16	None		153.5	19.5
							(1)	0.296	166.5	10.5
							(2)	0.227	165.0	8.0
V-4342	5.94	2.01	1.72	1.05	0.44	0.15	None		150.0	19.0
							(1)	0.265	159.5	12.0
							(2)	0.191	159.5	9.0
V-4249	5.95	2.04	1.84	0.50	0.29	0.11	None		134.5	28.0
							(1)	0.224	145.0	22.5
							(2)	0.213	142.5	22.0
V-4321	6.33	2.13	0.28	0.50	0.29	0.09	None		139.0	25.0
							(1)	0.318	148.5	18.0
							(2)	0.133	146.0	18.5
V-4292	6.13	1.98	0.45	1.12	0.28	0.10	None		134.0	29.5
							(1)	0.208	145.0	24.5
							(2)	0.115	144.0	21.0
V-4293	6.28	2.14	1.54	1.14	0.27	0.10	None		136.0	26.5
							(1)	0.093	148.0	17.5
							(2)	0.136	146.5	13.0
V-4294	6.10	2.12	2.34	1.12	0.31	0.10	None		135.5	22.0
							(1)	0.130	143.5	17.0
							(2)	0.196	149.0	10.5
V-4295	6.38	1.08	2.08	1.13	0.28	0.10	None		137.5	27.5
							(1)	0.096	142.0	19.5
							(2)	0.126	142.5	17.5
V-4296	5.60	3.14	2.09	1.07	0.30	0.10	None		137.5	26.5
							(1)	0.163	147.0	18.0
							(2)	0.137	145.0	14.5

[a] All specimens heat treated 1,950 F., 15 min., AC plus 1,300 F., 1 hr., AC.
[b] 1,000 F., 50 k.s.i., 144 hrs.
[c] 1,100 F., 25 k.s.i., 144 hrs.

Additionally, optical creep tests were performed on each heat in Table II to determine the time to reach 0.2% deformation. The results of these tests are shown in Table III.

As can be seen from both Tables II and III, several of the heats showed excellent combinations of room temperature strength, creep strength and retained ductility after creep exposure. The alloy having the best all-around

properties for use at temperatures up to 1100° F. was heat V–4293, which has a composition well within the commercial range of our preferred nominal composition.

The level of interstitial impurities and particularly oxygen must be considered in high temperature titanium base alloys. It is necessary to determine the amount of oxygen which can be tolerated without an excessive loss of post creep exposure ductility. In this regard, tests have been conducted on three nominal Ti-6.25Al-2Sn-1.5Zr-0.3Mo-1.0Bi-0.1Si alloys having different amounts of oxygen. The results of these tests are shown in Table IV.

TABLE IV

Effect of O_2 on creep stability [a]

Heat	Nominal O_2, percent	Creep [b] deformation, percent	U.T.S. (k.s.i.)	Y.S. (k.s.i.)	Percent RA
V–4293	0.1	NE	145.0	136.0	26.5
		0.093	156.5	148.0	17.5
V–4364	0.15	NE	159.5	148.5	21.5
		0.157	164.5	158.0	10.5
V–4363	0.20	NE	170.5	162.0	14.0
		0.095	172.0	169.0	0

[a] Heat treatment: 1,950 F., 15 min., AC plus 1,300 F., 1 hr., AC.
[b] Creep exposure: 1,000 F., 50 k.s.i., 144 hrs.

It is apparent from the percent RA in Table IV that an increase in oxygen from 0.1% to 0.15% causes an appreciable decrease in post exposure ductility and that an oxygen content of 0.2% makes the alloy brittle after creep exposure. Based upon this data, it has been determined that the oxygen content of our alloy should not exceed 0.12%.

Tests were also conducted at various temperatures to determine the short time elevated temperature strength of an alloy within the range of our invention. The results of these tests are shown in Table V.

TABLE V

Elevated Temperature Tensile Properties [a]
[Heat V–4198]

Test temperature (° F.)	U.T.S. (k.s.i.)	Y.S. (k.s.i.)	Percent RA
RT [b]	157.0	145.0	23.5
400	120.0	99.5	27.0
600	110.0	91.0	32.0
700	110.0	90.0	32.0
800	107.0	87.0	20.0
900	104.5	85.0	36.0
1,000	102.0	82.0	40.0
1,100	98.0	80.5	36.5
1,200	90.0	74.5	31.0

[a] Heat treatment: 1,950 F., 15 min., AC plus 1,300 F., 1 hr., AC.
[b] Room temperature.

The ultimate tensile strength and the yield strength of this alloy for short periods at elevated temperatures are excellent.

Notch tests were conducted on various alloys within our composition range to determine the notch toughness characteristics of the alloys. The results of these tests are shown in Table VI.

TABLE VI

Notch Properties [a]

Heat No.	Notch [b] tensile strength (k.s.i.)	Notched bar impact (ft.-lbs.)	Notch time fracture [c]	Notch time, [b] fracture, [c,d] after creep exposure
V–4264	221.0	31		Failed 1 min. at 230 k.s.i.
V–4263	214.5	30		Failed 2 mins. at 200 k.s.i.
V–4198	223.0	25	Failed 25 mins., 210 k.s.i.	Failed loading at 200 k.s.i.
V–4262	214.0	31		Failed 9 mins. at 210 k.s.i.
V–4300	214.5	30	Failed 2 hrs., 200 k.s.i.	Failed 50 mins. at 200 k.s.i.
V–4320	217.0	20	Failed 3 mins., 210 k.s.i.	
V–4249	210.5	31		
V–4293	215.0	25		

[a] Heat treatment: 1,950 F., 15 min., AC plus 1,300 F., 1 hr., AC.
[b] Notch acuity K_t, 8.
[c] Loaded 5 hours at 150 k.s.i.—load increased 10 k.s.i. every 5 hours to failure.
[d] Samples given 1,000 F. creep exposure, then notch machined after exposure.

An important factor in obtaining the optimum combination of properties for elevated temperature applications in titanium base alloys within our novel composition range is the manner in which an article formed from the alloy is heat treated. In treating articles made from an alloy in accordance with our invention, the first step should be either a beta anneal or beta working. This should be followed by an intermediate anneal relatively low in the alpha-beta phase region which, in turn, may be followed by aging. The effects of exemplary heat treatments consisting of heating the metal above its beta transus temperature, annealing within the alpha-beta phase region, with and without subsequent aging, are shown for a Ti-6Al-2Sn-2Zr-1Mo-0.35Bi-0.12Si alloy in Table VII.

TABLE VII

Heat treatment	Creep [a] deformation, percent	U.T.S. (k.s.i.)	Y.S. (k.s.i.)	Percent RA	Percent Elong. [c]	Notch bar impact (ft.-lbs.)
1,900 F., 15 min., AC plus 1,700 F., 1 hr., AC	NE [b]	144.0	128	26.0	15	32.0
	0.234	157.0	147	12.5	11	
1,900 F., 15 min., AC plus 1,700 F., 1 hr., AC plus 1,100 F., 8 hrs., AC	NE	154.5	143	18.0	14	27.5
	0.136	157.0	149	13.0	11	
1,900 F., 15 min., AC plus 1,500 F., 1 hr., AC	NE	145.0	138	26.0	12	27.0
	0.190	154.0	148	16.0	12	
1,900 F., 15 min., AC plus 15,—F., 1 hr., AC plus 1,100 F., 8 hrs., AC	NE	152.0	150	16.0	12	21.5
	0.111	156.0	151	18.0	12	
1,900 F., 15 min., AC plus 1,300 F., 1 hr., AC	NE	146.5	139	26.0	14	26.0
	0.120	155.0	148	19.0	12	
1,900 F., 15 min., AC plus 1,300 F., 1 hr., AC plus 1,100 F., 8 hrs AC	NE	154.0	146	19.0	12	21.0
	0.106	159.0	152	16.0	13	
1,900 F., 15 min., cool at 250 F./hr. to 1,300 F., AC plus 1,100 F., 8 hrs., AC	NE	146.0	139	14.0	10	27.0
	0.086	148.0	145	7.0	2	

[a] Creep exposure: 1,000 F., 50 k.s.i., 144 hrs.
[b] Not exposed.
[c] One inch gauge length.

Table VII shows that the heat treatment for the best combination of creep resistance, post exposure ductility and notch bar impact properties is a beta anneal at 1900° F. followed by cooling at an intermediate rate and an anneal at 1300° F., which is low in the alpha-beta field, followed by aging at 1100° F. for eight hours with an air cool.

The preferred heat treatment for an article of an alloy according to our invention consists in working or annealing at a temperature above the beta transus temperature of the alloy which is approximately 1850° F., cooling at an intermediate rate and annealing at a temperature low in the alpha-beta field, i.e. from about 1300° F. to about 1500° F. This treatment may be followed by aging at a temperature within the range of about 900° F. to about 1200° F. depending upon the specific properties desired.

Our invention has important features which include good creep resistance and post exposure ductility along with good notch bar impact and tensile properties.

While we have shown and described preferred embodiments of our invention, it is to be understood that the invention may be otherwise embodied within the scope of the following claims.

We claim:

1. A titanium base alloy consisting essentially of about: 5.9 to 6.75% aluminum, 1.5 to 2.5% tin, 0.5 2.0% zirconium, 0.8 to 2.0% molybdenum, 0.15 to 0.6% bismuth, 0.07 to 0.18% silicon, up to 0.12% oxygen, up to 0.2% carbon, up to 0.1% nitrogen, balance titanium; said alloy being characterized by good creep resistance and good post creep ductility at temperatures up to about 1100° F.

2. An alloy as set forth in claim 1 having 6.25% aluminum, 2.0% tin, 1.5% zirconium, 1.0% molybdenum, 0.35% bismuth, 0.1% silicon, less than 0.1% oxygen, balance titanium.

3. An alloy as set forth in claim 1 wherein the total of oxygen plus nitrogen plus carbon is less than 0.2%.

4. An alloy as set forth in claim 1 wherein the aluminum, tin, zirconium and silicon are present in the following relationship:

$$\text{Percent tin}/3+\frac{\text{percent zirconium}}{6}+\text{percent silicon}\times 4\leqq 8$$

5. A process for treating articles for elevated temperature applications of a titanium base alloy consisting essentially of 5.9 to 6.75% aluminum, 1.5 to 2.5% tin, 0.5 to 2.0% zirconium, 0.8 to 2.0% molybdenum, 0.15 to 0.6% bismuth, 0.07 to 0.18% silicon, up to 0.12% oxygen, up to 0.2% carbon, up to 0.1% nitrogen, balance titanium; said process comprising heating said article to a temperature above the beta transus temperature of said alloy, cooling said article at an intermediate rate and annealing said article to a temperature low in the alpha-beta field.

6. A process as set forth in claim 5 wherein said article is heated to a temperature above about 1850° F. and annealed at a temperature between about 1300° F. and about 1500° F.

7. A process as set forth in claim 5 including cooling said article after said anneal and aging the cooled article at a temperature between about 900° F. and about 1200° F.

8. A process as set forth in claim 7 wherein said article is aged at a temperature of about 1100° F. for about eight hours.

9. A process as set forth in claim 7 wherein said article is heated above about 1850° F., annealed at 1300° F., aged at 1100° F. for eight hours and air cooled.

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CHARLES N. LOVELL, Primary Examiner

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,756,810 Dated September 4, 1973

Inventor(s) Warren M. Parris and Donald B. Hunter

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 1, Line 35, After "strength" insert --and the creep strength--.
Col. 1, Line 55, After "based" insert --upon--.
Table II, Col. 3, Heat V-4292, Under the formula Al, "6.13" should read --6.23--.
Col. 5, Line 22, Change "0.3 Mo" to --1.0 Mo--.
Col. 5, Line 23, Change "1.0 Bi" to --0.3 Bi--.
Claim 1, Col. 7, Line 3, "0.5 2.0% zirconium" should read --0.5 to 2.0% zirconium--.
Claim 4, Col. 7, Line 19, Before "Percent tin/3" insert --Percent aluminum +--.

Signed and sealed this 19th day of February 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
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FORM PO-1050 (10-69)

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