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STABLE, HIGH STRENGTH, ALPHA TITANIUM BASE ALLOYS

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This invention pertains to strong, ductile and thermally stable, alpha alloys of titanium, which are characterized by high strength and ductility at both room and elevated temperatures, and which retain these properties on prolonged exposure to elevated temperatures in both stressed and unstressed conditions.

We have previously shown in Patents 2,669,513; 2,669,514; 2,703,278; and 2,779,677, that alpha titanium alloys containing aluminum, tin and antimony singly and in combination, have excellent strength and ductility properties over the ranges of about 0.5–8% aluminum, 1–23% tin and 1–18% antimony.

Our original investigations indicated that the aforesaid alloys containing any one or more of aluminum, tin and antimony within the ranges aforesaid, were all single phase, alpha alloys. We have now discovered that under certain conditions, an ordered or partially ordered arrangement of the titanium and alloy atoms is obtained in alloys containing one or more of these elements aluminum, tin and antimony in amounts above a certain critical upper limit. Our investigations indicate that this ordered structure results from the formation of a Ti_3Al phase, a Ti_3Sn phase, a Ti_3Sb phase, or if more than one alpha stabilizer of this group is present, the aluminum, tin and antimony combine to form a Ti_2Al, Sn, Sb) phase. That is to say, when any two or more of aluminum, tin and antimony are present in the alloy, the atoms of these elements will appear indiscriminately and in random sequence in the ordering, without affecting the building up of the ordered structure. The composition of the completely ordered structure thus corresponds to Ti_3Al, Ti_3Sn, Ti_3Sb, if these elements are present individually, or to Ti_3(Al, Sn, Sb) if any two or more are present, and occurs at about 25 atomic percent of these alloying additions, or at about 16, 45 and 46 weight precent, for Al, Sn and Sb, respectively.

The conditions under which this ordered phase starts to form are prolonged exposure at elevated temperatures of about 800–1000° F. Strain caused by stress appears to accelerate the formation of this ordering, particularly where the material is stressed at elevated temperatures on the order of 800–1000° F.

For titanium-aluminum binary alloys, our investigations have shown that this ordering becomes sufficiently pronounced markedly to decrease ductility during aging, at around 6 to 8% by weight of aluminum, i.e., at about 6–7% aluminum if the aging is conducted at around 800° F. and at about 7–8% aluminum if the aging is effected at about 1000° F. In the case of titanium-tin and titanium-antimony binary alloys, the ordering tendency becomes pronounced at about 22–27 weight percent of the tin and/or antimony.

Our investigations have further shown that insofar as concerns their effects on this tendency toward ordering, about 3% by weight of tin or antimony is equivalent to about 1% by weight of aluminum. Thus, where two or all of these elements are present, the equivalent aluminum content for purposes of computing the ordering tendency is equal to the sum of the aluminum content plus ⅓ times the tin content plus ⅓ times the antimony content, considered on a weight percent basis. Thus the ordering tendency will become pronounced if the equivalent aluminum content of the alloy, computed in this manner, is upwards of about 7%, where any one, two or all of the elements aluminum, tin and antimony are present in the alloy. Or expressed more exactly in terms of atomic precent, the ordering becomes pronounced at 800° F. if the total atomic percent of the aluminum, tin and antimony present in the alloy is upwards of about 10.5 atomic percent and at 1000° F. if the total atomic percent of these elements is upwards of about 12.5 atomic percent.

The formation of this ordered structure causes a loss in ductility of these alloys. Although the alpha alloys of the above patents have, in the condition as annealed above the maximum temperature at which ordering occurs or as quenched to room temperature therefrom, excellent strength and ductility at room temperature, nevertheless if these alloys containing above the critical aluminum equivalent content aforesaid, are subjected to prolonged service at temperatures around 800–1000° F., loss in ductility will occur. And since the strength of these alloys is dependent on the total alloy content, the maximum strength of these Ti-(Al, Sn, Sb) alloys, suitable for use at temperatures of 800–1000° F. will be limited by the maximum or critical equivalent aluminum content aforesaid.

Now we have discovered, in accordance with one aspect of our present invention, that zirconium additions to alpha alloys containing one or more of aluminum, tin and antimony, will produce strengthening of these alloys without promoting the formation of the ordered Ti_3(Al, Sn, Sb) type of phase, so long as the equivalent aluminum content is less than 6% by weight or less than 10.5 atomic percent of the alloy. Therefore, the maximum strength obtainable in a stable alpha alloy of this type will be greater for alloys containing zirconium than for those in which no zirconium is present. The zirconium added to such alpha alloys replaces part of the titanium in the Ti_3(Al, Sn, Sb) compound, which can thus be expressed as $(Ti, Zr)_3$(Al, Sn, Sb), and does not alter significantly the critical equivalent aluminum content of 7 weight percent at which ordering becomes pronounced. Thus, for example, we have found that a Ti—4A1—12Sn alloy, the equivalent aluminum content of which as above computed, is 8.0% by weight, is unstable; while a Ti—4A1—12Zr alloy having an equivalent aluminum content of 4% by weight is stable; and also that a Ti—6A1—6Zr alloy having an equivalent aluminum content of 6% by weight is stable.

In our discussion thus far, we have confined attention to the alpha promoters aluminum, tin and antimony which enter the ordered position X in the ordered phase Ti_3X, and to zirconium, which substitutes, as noted above, for part of the titanium in the ordered phase and hence does not promote ordering. Additional alpha promoters which enter the ordered position X when they dissolve in alpha titanium are silver and indium, which thus up to the limits of their solubilities in alpha titanium, are susceptible to the formation of ordered phases of the type Ti_3Ag, and Ti_3In. Indium is soluble in alpha titanium up to about 3% by weight, and silver up to about 10% by weight. Within these limits of alpha solubility, additions of these elements will therefore increase the strength of alpha titanium alloys, but if ordering embrittlement is to be avoided, silver and indium like aluminum, tin and antimony, must not be present in the alloy in total amount of more than about 10.5 atomic percent.

Additional elements which, like zirconium, do not enter the ordered position X in the Ti_3X lattice, and therefore do not contribute to ordering, but which at the same time, produce strengthening of alpha titanium alloys, up to the limits of their alpha solubilities therein, are hafnium, and the various beta promoters such as vanadium, columbium, tantalum, molybdenum, manganese, iron, chromium, tungsten, cobalt, etc. Only a few of these beta promoters, however, have sufficient solubility in alpha titanium to impart material strengthening to alpha titanium alloys. They are tantalum which is alpha soluble up to about 10% by weight, columbium and vanadium which are alpha soluble up to about 3% by weight, and molybdenum and manganese which are alpha soluble up to about 0.5% by weight of each. The alpha solubilities of beta promoters like chromium, tungsten, iron, cobalt, nickel, copper and silicon are so low as not to permit of significant amounts of strengthening of alpha titanium alloys, but to the extent that these elements are soluble in alpha titanium, they will act like zirconium in that they will permit equivalent strengthening by substituting for part of the titanium and will not take up ordered positions in the lattice.

Since zirconium and hafnium are isomorphous with titanium, and produce only alpha alloys therewith at room or atmospheric temperature, they may accordingly be substituted for titanium in all proportions. A preferred range for zirconium as an alpha strengthener is, however, about 4 to 15%.

Thus to summarize, the general formula for the completely ordered structure with reference to those of the elements above mentioned which have appreciable solubilities in alpha titanium is as follows:

$$(Ti, Zr, Hf, V, Cb, Ta, Mo, Mn)_3(Al, Sn, Sb, Ag, In)$$

All elements in the above formula must, as stated, be present only within the limits of alpha solubility for each or in total amount in the production of a high strength, alpha alloys of titanium. Furthermore, if ordering embrittlement of the alloy due to aging at 800–1000° F. is to be avoided, the total content of the elements which take up ordered positions in the Ti_3X lattice, namely, those which substitute for X therein, shall not exceed 10.5 atomic percent of the total alloy content, these being, as above stated, the elements aluminum, tin, antimony, silver and indium.

Since the atomic weights of tin, antimony, silver and indium are close to one another, falling within the range of about 115–122 in round numbers, they will have approximately the same effect on the ordering tendency when alloyed with titanium, on an equal weight percent basis, i.e., percent-for-percent of each. And since as shown above, the equivalent aluminum content of tin and antimony on a weight percent basis is approximately ⅓ times the weight percent of each present in the alloy, the same rule applies for silver and indium. Thus the general formula for the equivalent aluminum content on a weight percent basis is the sum of the aluminum content plus ⅓ times the total weight percent of tin, antimony, silver and indium present in the alloy. If the equivalent aluminum as thus computed is under 6%, the alloy is stable, and if over 7% the alloy is unstable. The critical limit of 6 weight percent of equivalent aluminum corresponds to the critical limit of 10.5 atomic percent of these elements present.

Since the alloying additions are usually given in terms of weight percent of each, the conversion to atomic percent for determining the ordering tendency is computed from the fraction in which the sum of the weight percent divided by the atomic weight of each of Al, Sn, Sb, Ag and In, appears in the numerator, while the sum of the weight percent divided by the atomic weight of each and every element present in the alloy appears in the denominator. If the fraction as thus computed is under 0.105, i.e., under 10.5 percent, the alloy is stable and if above this amount, the alloy is unstable.

As illustrative of the invention as thus described, reference will now be had to the test results in the following Table I, based on a series of alloy ingots produced by arc melting titanium sponge of commercial purity except as otherwise indicated, together with the alloying ingredients, in a cold mold furnace, in an inert atmosphere. The ingots were forged into plate at about 2000° F., and rolled into sheet or bar stock at about 1600° F. finishing temperature, were then annealed 7 hours at 1600° F. and air cooled to room temperature. As shown by the data in the table, bar or sheet specimens, as indicated, of each of the alloys as thus produced, were tested for room temperature tensile properties in the "as annealed" condition, and also after aging exposure for at least 100 hours at 800° F. and 1000° F., in unstressed and/or stressed condition as shown. The alloys were also tensile tested at 1000° F., with results as shown in the table.

TABLE I

Composition, Percent (Balance Titanium)	Specimen Type	Time, Hrs.	Temp., F.	Stress, 1,000 p.s.i.	Percent Plastic Strain	Min. Creep Rate per hr.	Test Temp., F.	Tensile Properties, p.s.i. × 1,000		Percent Elongation in 1"	Percent Reduction in Area	MBR, T	
								0.2% Offset Yield	Ult. Str.			L	T
6Al—6Sn, RES-1435-15 (Iodide base).	Bar (T)	None					75	103	113	22	47		
		118	800	None			75	113	114	20	48		
		138	800	65	4.82	0.00004	75	117	119	8	20		
		120	1,000	None			75	114	114	8	17		
		None					1,000	58	66	30	35		
6Al-6Sn, RES-1435-16 (sponge base).	Bar (T)	None					75	116	119	10	13		
		118	800	None			75	113	123	10	14		
		138	800	65	1.34	0.0005	75	120	121	4	12		
		120	1,000	None			75	118	120	2	8		
		None					1,000	62	72	36	36		
6Al—6Sn-0.15 Ox, RES-1435-17.	Bar (T)	None					75	128	129	4	3		
		118	800	None			75		126	4	7		
		120	800	65	0.09	Nil	75		83	0	3		
		120	1,000	None			75		125	0	0		
		None					1,000	66	79	32	48		
6Al-6Sn—0.3Ox, RIN-1016 R2[a].	Bar (L)	None					75		124	1	3		
	Bar (T)	None					75		125	1	3		
	Bar (L)	100	1,000	None			75		119	2	1		
	Bar (T)	100	1,000	None			75		89	2	1		
	Bar (L)	None					75		87	1	0		
	(T)	None					75		75	1	0		
	Bar (L)	100	1,000	None			75		89	0	2		
	Bar (T)	100	1,000	None			76		60	0	0		
6Al—6Sn—0.075N, RES-1435-18.	Bar (T)	None					75	139	139	2	6		
		118	800	None			75		139	4	6		
		120	800	65	0.34	0.0004	75		106	0	3		
		120	1,000	None			75		95	0	3		
		None					1,000	61	73	24	39		

TABLE I—Continued

Composition, Percent (Balance Titanium)	Specimen Type	Time, Hrs.	Temp., F.	Stress, 1,000 p.s.i.	Percent Plastic Strain	Min. Creep Rate per hr.	Test Temp., F.	Tensile Properties, p.s.i. × 1,000		Percent Elongation in 1"	Percent Reduction in Area	MBR, T	
								0.2% Offset Yield	Ult. Str.			L	T
		None					75	129	131	12	12		
		118	800	None			75	127	131	4	8		
6Al-6Sn—0.075C, RES-1435-19.	Bar (T)	120	800	65	(1)	(1)	75		132	6	14		
		120	1,000	None			75		132	0	5		
		None					1,000	66	76	42	45		
		None					75	129	134	8	11		
		118	700	None			75		133	4	6		
6Al-6Sn—0.5Fe, RES-1435-20.	Bar (T)	120	800	65	(1)	(1)	75		128	2	9		
		120	1,000	None			75	135	136	3	6		
		None					1,000	73	89	20	40		
		None					75	134	145	15	31		
6Al—6Sn—1Mo, RES-1435-29.	Bar (T)	96	800	65	0.128	0.0013	75	129	140	4	8		
		97	1,000	15	0.145	0.0009	75	140	147	8	15		
		None					1,000	79	88	12	59		
		None					75	129	134	14	39		
		None					75	125	130	11	44		
6Al—6Sn—2V, RES-1435-30.	Bar (T)	97	800	65	0.106	0.0011	75	129	130	2	9		
		100	1,000	15	0.005	0.0005	75	135	135	6	7		
		None					1,000	70	80	18	35		
		None					75	114	117	30	31		
		95	800	65	0.375	0.0004	75		121	14	15		
6Al—6Sn—3Cb, RES-1435-31.	Bar (T)	113	1,000	15	0.010	0.0004	75	120	121	8	17		
		None					1,000	61	67	15	38		
6Al—3Sn—3Sb, PA-2210.	Sheet (L)	None					75	110	113	12	24		
		None					75	131	131	2	6		
		118	800	None			75		130	2	12		
6Al—3Sn—3Sb, RES-1435-21.	Bar (T)	120	800	65	(1)	(1)	75		126	1	2		
		None					1,000	77	83	10	34		
4Al—4Sn—10Zr, PA-2212.	Sheet (L)	None					75	126	133	1	2		
		None					75	124	129	20	38	3.1	3.0
		118	800	None			75	126	132	24	40		
4Al—3Sn—10Zr, RES-1435-23.	Bar (T)	120	800	65	(1)	(1)	75	127	133	14	11		
		120	1,000	None			75	126	133	12	40		
		None					1,000	66	84	22	48		
		None					75	114	120	28	36	6.7	9.0
		98	800	65	0.624	0.0021	75	116	119	12	13		
4Al—12Zr, RES-1435-24.	Bar (T)	114	800	65	0.741	[b] 0.0009	75	117	120	18	24		
		96	1,000	15	0.150	0.0011	75	116	119	18	35		
		97	1,000	15	0.175	[b] 0.0014	75	116	118	22	37		
		None					1,000	60	69	16	44		
		None					75	118	122	15	31	3.9	2.7
		100	800	65	0.190	Nil	75	122	123	8	18		
5Al—5Sn—5Zr, RES-1435-25.	Bar (T)	100	800	65	0.399	[b] Nil	75	125	125	4	9		
		97	1,000	15	0.010	[b] 0.001	75		124	12	39		
		None					1,000	64	78	25	49		
		None					75	128	136	29	43	3.3	2.5
		138	800	65	0.306	0.0009	75	128	129	2	8		
5Al—5Sn—10Zr, RES-1435-26.	Bar (T)	96	800	65	1.010	[b] 0.0008	75	137	138	23	31		
		98	1,000	15	0.065	[b] 0.0006	75	133	140	18	31		
		None					1,000	76	93	26	40		
		None					75	128	130	18	20	3.6	2.0
		118	800	65	0.140	0.0008	75		126	3	9		
6Al—6Sn—6Zr, RES-1435-27.	Bar (T)	95	800	65	0.086	[b] Nil	75	132	132	8	10		
		97	1,000	15	0.025	[b] 0.0001	75	132	133	4	5		
		None					1,000	79	89	30	32		
		None					75	113	115	23	38	2.6	2.6
		100	800	65	4.420	0.0006	75	113	113	11	26		
6Al—6Zr, RES-1435-28.	Bar(T)	112	800	65	10.000	[b] Nil	75	104	104	16	47		
		99	1,000	15	0.028	[b] 0.005	75	117	118	14	31		
		None					1,000	55	67	30	35		
		None					75	134	145	15	31	2.3	3.5
		96	800	65	0.128	0.0013	75	129	140	4	8		
6Al—6Sn—1Mo, RES-1435-29.	Bar(T)	111	800	65	0.255	[b] 0.0010	75	127	140	12	20		
		97	1,000	15	0.145	[b] 0.0009	75	140	147	8	15		
		None					1,000	79	88	12	59		
		None					75	129	134	14	39	2.9	3.0
		97	800	65	0.106	0.0011	75	127	130	2	9		
6Al—6Sn—2V, RES-1435-30.	Bar(T)	100	1,000	15	0.005	[b] 0.0005	75	135	135	6	7		
		None					1,000	70	80	18	35		
		None					75	114	117	30	31	2.6	3.3
		95	800	65	0.375	0.0004	75		121	14	15		
6Al—6Sn—3Cb, RES-1435-31.	Bar(T)	97	800	65	0.300	[b] 0.0006	75	116	118	10	24		
		113	1,000	15	0.010	[b] 0.0003	75	120	121	8	17		
		None					1,000	61	67	15	38		
		None					75	140	148	20	51		
5Al—2.5Sn (Sponge Base-High in Interstitials)	Sheet(L)	71	800	50	0.36	0.004	75	147	158	20	37		
		112	1,000	15	1.54	0.012	75	132	142	15	36		
		None					75	134	142	14	20		
		104	800	60	0.06	[b] 0.0003	75	137	146	7	15		
4Al—12Zr—3Cu, RES-1435-41-47, inc.	Bar(T)	98	800	65	0.09	0.0006	75	137	145	10	18		
		104	1,000	10	0.10	[b] 0.0005	75	135	143	9	18		
		99	1,000	15	0.19	0.0012	75	134	141	12	20		
		None					75	150	157	12	21		
		97	800	65	0.079	[c] Nil	75	151	162	7	9		
5Al—12Zr—6Cu, RES-1335-40.	Bar(T)	98	1,000	25	0.436	[c] 0.0033	75	150	159	12	10		
		69	1,000	15	0.056	[c] 0.0016	75	146	156	10	23		
		99	800	75	0.105	[c] 0.0060	75	151	161	10	10		
(average values)	Bar(L)	None					1,000	90	108	28	60		
		None					75	128	139	19	17		
		118	800	None			75	137	143	4	8		
6Al—6Zr—3Cu, RES-1435-34.		117	800	65	0.153	0.0003	75		136	0	0		
		120	1,000	None			75	139	149	12	16		
		98	1,000	15	0.130	[c] 0.0012	75	141	154	14	12		
		None					75	118	128	10	14		
		118	800	65	0.175	0.0005	75		117	4	11		
4Al—6Sn—6Sb, RES-1435-22.	Bar(T)	112	1,000	15	0.060	0.0060	75	128	130	4	9		
		None					1,000	70	80	13	27		

[a] Scale-up ingot.
[b] 0.010" of metal was removed from diameter of reduced section after creep exposure (original diameter 0.125").
[c] 0.025" of metal was removed from diameter of reduced section after creep exposure (original diameter 0.125").
[1] Not measured.

As shown by the test results in the foregoing table, it will be seen that all analyses having equivalent aluminum of 6 or under on a weight percent basis, showed excellent stability after creep exposure for approximately 100 hours at 800° F. and 65,000 p.s.i., and at 1000° F. and 15,000 p.s.i. stress, such, for example, as the Ti—5Al—2.5Sn, Ti—4Al—12Zr, Ti—6Al—6Zr and Ti—4Al—4Sn—10Zr analyses. In contrast, all of the analyses containing equivalent aluminum of more than 6 showed instability in varying degrees as a result of such aging and creep exposure tests, such for example, as the Ti—6Al—6Sn analyses with and without other additions, as indicated, and the Ti—5Al—5Sn—5Zr, Ti—5Al—5Sn—10Zr and Ti—4Al—6Sn—6Sb analyses.

Referring to the stable alloys of the first group, the Ti—5Al—2.5Sn alloy retained excellent ductility of 15–20% tensile elongation before and after all exposure tests, combined with a high tensile strength of 140,000–160,000 p.s.i. The same is true of the Ti—4Al—12Zr and Ti—6Al—6Zr alloys which maintained tensile elongations of 12–22% and 11–16% after exposure. Similarly, the Ti—4Al—4Sn—10Zr alloy maintained excellent tensile elongation of 12–24% before and after creep exposure with an ultimate strength of about 130,000 p.s.i.

The copper-bearing analyses containing equivalent aluminum under 6 were not quite so stable as those above discussed, because copper reacts with the titanium to form the compound Ti_2Cu, which thus increases the percentage of aluminum or its equivalent present in the remaining alpha matrix, and which also tends to precipitate out during aging exposure and thus tends to reduce ductility. Copper, however, has a marked strengthening action on the alloy as shown by the ultimate strengths varying from about 140,000 to 160,000 p.s.i. for the Ti—12Zr—3Cu and the Ti—6Al—6Zr—3Cu alloys. These alloys also having excellent creep strength as shown in the table. Likewise, the Ti—5Al—12Zr—6Cu alloy in addition to extremely high strength of about 160,000 p.s.i. has quite good stability, with tensile elongations maintained being about 10–12% before and after creep exposure.

All rapidly eutectoid compound-forming elements, such as cobalt, nickel, silicon, beryllium, etc., have the same effect as copper, in that they react with and tie up some of the titanium, thereby to increase the atomic percentage of aluminum and equivalent atoms present in the alpha matrix.

The effect of the various interstitial and beta promoter additions within the limits of alpha-solubility, as shown in the table, is somewhat masked by the fact that these additions were made in each instance to the Ti—6Al—6Sn base alloy containing equivalent aluminum of 8% and hence above the limit of 6 for stability, the base alloy itself being unstable for this reason as shown by the Ti—6Al—6Sn analyses containing no such additions. It will be seen, however, by comparison that alpha soluble

columbium additions, improve ductility of this base alloy on aging. Thus such columbium additions improve stability even for these alloys containing up to 7 or 8% by weight of equivalent aluminum.

Alpha soluble vanadium additions have the same stabilizing action. Thus a Ti—12Sn—4A1 alloy containing the 8% aluminum equivalent had in the as quenched condition from 1500° F., a tensile elongation of 4% and an area reduction of 3%, which values were reduced to zero on aging for 100 hours at 1000° F. In contrast, a Ti—12Sn—4A1—2V alloy had as quenched from 1500° F., a tensile elongation of 10% and an area reduction of 18%. On aging for 200 hours at 1000° F., the tensile elongation was found to be 10% and the area reduction 22%. Thus the alpha soluble addition of 2% vanadium to the Ti—12Sn—4A1 base alloy transformed it from a highly unstable to a highly stable alloy. Other tests have shown that alpha soluble molybdenum and tantalum additions impart a similar stabilizing action.

As to the interstitial additions, carbon, oxygen and nitrogen, it will be seen from Table I that they have a generally detrimental effect on stability, and hence are not desirable additions to alpha alloys as adjudged from this standpoint, despite the increase in strength imparted thereby.

The alloys of the invention have good welding properties as shown by the test results in the following Table II:

TABLE II

Bend-test results for alpha alloys before and after welding

[Annealed 4 hours at 1600° F. and air cooled.]

Alloy No.	Composition, percent (Balance Titanium)	Minimum Bend Radius, T, Longitudinal	
		Base	Welded
RES-1435-23	4Al—4Sn—10Zr	3.1	7.2
PA-2212	4Al—4Sn—10Zr	5.2	5.3
RES-1435-24	4Al—12Zr	6.7	4.0
PA-2213	4Al—12Zr	3.5	6.8
RES-1435-25	5Al—5Sn—5Zr	3.9	4.0
PA-2214	5Al—5Sn—5Zr	2.5	7.4
RES-1435-26	5Al—5Sn—10Zr	3.3	5.8
PA-2215	5Al—5Sn—10Zr	4.6	8.0
RES-435-27	6A1—6Sn—6Zr	3.6	5.3
PA-2216	6A—6Sn—6Zr	4.4	7.6
RES-1435-28	6Al—6Zr	2.6	2.3
PA-2217	6Al—6Zr	2.6	3.7
RES-1435-29	6Al—6Sn—1Mo	2.3	6.7
RES-1435-30	6Al—6Sn—2V	2.9	5.8
RES-1435-31	6Al—6Sn—3Cb	2.6	5.2
PA-2210	6Al—3Sn—3Sb	3.0	7.6
PA-2211	4Al—6Sn—6Sb	3.5	8.0

The room temperature mechanical properties of additional Ti—Al—Zr alloys according to the invention as annealed at 1600° F. are given in the following Table III; while the microstructures of these alloys as annealed at 1600° F. are given in the succeeding Table IV. This table also gives the 100-hour, 800° F. bend-creep and bend-creep-bend test results for this same group of alloys.

TABLE III

Hardness, bend, and room-temperature longitudinal sheet tensile test results for Ti—Al—Zr *alpha alloys*

[Annealed 7 hours at 1600° F. and air cooled to room temperature.]

Alloy Number	Composition, percent (Balance Titanium)	Tensile Properties: p.s.i.×1,000		Percent Elongation in 1″	Percent Reduction in Area	VHN	MBR, T (Long.)
		0.2% Offset Yield	Ultimate Strength				
PA-2240	4Al—6Zr	89	94	15	37	310	3.9
PA-2241	4Al—12Zr	106	112	13	24	347	4.0
PA-2242	4Al—18Zr	108	114	6	10	387	4.4
PA-2243	4Al—24ZR	116	119	2	6	374/405	5.7
PA-2244	4Al—6Zr	99	105	20	28	351	3.7
PA-2245	5Al—12Zr	118	121	5	7	365	4.7
PA-2246	5Al—18Zr	127	129	3	6	405	2.5/Br
PA-2247	5Al—24Zr	132	133	1	5	396	Br
PA-2248	6Al—6Zr	111	115	13	27	386	3.9
PA-2249	6Al—12Zr	122	123	15	35	393	4.2
PA-2250	6Al—18Zr	131	131	9	20	416	4.2
PA-2251	6Al—24Zr		125	1	3	417/472	Br

TABLE IV

800° F. bend-creep results and hardness and bend test results before and after bend-creep exposure on Ti—Al—Zr *alloys. Structure as annealed*

[Annealed 7 hours at 1600° F. and air cooled to room temperature.]

Alloy number	Composition, percent (Balance Titanium)	Before Exposure			100-Hr. 800° F. Exposure		
		Structure [1]	VHN	MBR, T (Long.)	Residual Stress, 1,000 p.s.i.	VHN	MBR, T (Long.)
PA-2240	4Al—6Zr	Trace B	310	3.9	33	316	2.2
PA-2241	4Al—12Zr	Trace B	347	4.0	46	354	8.8
PA-2242	4Al—18Zr	Approx. 5B	387	4.4	52	358	Br
PA-2243	4Al—24Zr	Approx. 15B	374/405	5.7	64	386	Br
PA-2244	5Al—6Zr	Trace B	351	3.7	49	346	3.8
PA-2245	5Al—12Zr	Trace B	365	4.7	----	----	----
PA-2246	5Al—18Zr	Approx. 4B	405	2.5/Br	----	----	----
PA-2247	5Al—24Zr	Approx. 10B	396	Br	----	----	----
PA-2248	6Al—6Zr	Trace B	386	3.9	----	----	----
PA-2249	6Al—12Zr	Trace B	393	4.2	----	----	----
PA-2250	6Al—18Zr	Approx. 4B	416	4.2	64	396	Br
PA-2251	6Al—24Zr	Approx. 10B	417/472	Br	----	----	----
PA-2220 [2]	4Al—6Zr—3Cu	C	335	5.2	48	344	4.9
PA-2230 [2]	4Al—6Zr—6Cu	C	319	Br	50	332	9.6
PA-2231 [2]	4Al—12Zr—3Cu	C	330	4.7	54	341	4.4
PA-2218 [2]	4Al—12Zr—6Cu	C	364	Br	56	363	Br

[1] B=beta, C=compound. All the Ti—Al—Zr compositions are predominantly equiaxed alpha structures having the beta phase intergranularly in the described amounts. The Ti—Al—Zr—Cu compositions have both equiaxed and acicular alpha in addition to the compound phase.

[2] These data have been included to show the effects of a dispersoid addition on the Ti—4Al—(6, 12) Zr base. The alloys have been annealed 24 hours at 1400° F., furnace cooled to 1100° F., held 16 hrs. at 1100° F., and air cooled to room temperature.

The beta stabilizing effect of zirconium is demonstrated by the structures observed for this group of Ti—Al—Zr alpha alloys. The 1600° F. annealing temperature resulted in a two-phase structure. This varies from traces of beta phase for 6 to 12% zirconium contents, to 15% beta phase for 24% zirconium content, in a predominantly equiaxed alpha structure. The beta is located at grain corners and intergranularly.

The foregoing data of Table I also shows that elevated-temperature strength as well as the room-temperature strength of the Ti—Al—Zr alloys is increased with increasing aluminum or zirconium content. Aluminum appears to be about five or six times as potent as zirconium at room temperature on a weight percentage basis. A decrease in ductility accompanies the increase in strength. In the 800° F. bend-creep tests of Table III, the aluminum additions again appear to be about five or six times as effective as zirconium as an alpha strengthening agent. The bend-creep-bend tests indicate that the most highly alloyed compositions are embrittled during the 100-hour, 800° F. exposure.

The alloys of the invention also have good oxidation resistance at temperatures up to about 1800° F. and reasonably good oxidation resistance at about 1900° F. as shown by the test results in Table V below. The data in the lower portion of this table on unalloyed titanium and on titanium-tin and titanium-tin-aluminum alloys is added for comparison.

TABLE V

Oxidation test data for alpha alloys

Composition, Percent (Balance Titanium)	Weight Gain, mg./cm.^{2}				
	24—1,560° F [a]	4—1,600° F [b]	24—1,600° F [c]	4—1,800° F [d]	4—1,920° F [e]
4Al—4Sn—10Zr, RES-1435-23 [f]	6.4	3.1	6.0	10.5	64
4Al—12Zr, RES-1435-24	6.1	3.1	7.5	9.6	35
5Al—5Sn—5Zr, RES-1435-25	5.3	1.9	5.8	9.2	51
5Al—5Sn—10Zr, RES-1435-26	4.9	3.1	9.3	13.9	35
6Al—6Sn—6Zr, RES-1435-27	4.6	2.6	7.5	12.5	53
6Al—6Zr, RES-1435-28	3.8	2.4	6.4	10.3	28
6Al—6Sn—1Mo, RES-1435-29	9.0	8.3	24.3	18.9	44
6Al—6Sn—2V, RES-1435-30	15.1	4.3	34.5	20.1	34
6Al—6Sn—3Cb, RES-1435-31	2.5	1.8	3.6	3.7	8
Unalloyed, A-39	14.0	----	----	----	35
4Al, A-42	12.0	----	----	----	----
8Al, A-43	8.5	----	----	----	----

[a] Exposed in still air for 24 hrs. at 1,560° F. and air cooled to room temperature.
[b] Exposed in still air for 4 hrs. at 1,600° F. and air cooled to room temperature.
[c] Specimens from (b) above exposed an additional 20 hrs. at 1,600° F. and air cooled to room temperature.
[d] Exposed in still air for 4 hrs. at 1,800° F. and air cooled to room temperature.
[e] Exposed in still air for 4 hrs. at 1,920° F. and furnace cooled to room temperature.
[f] Alloy number.

It will be noted from the above data that the addition of about 3% columbium imparts excellent oxidation resistance up to at least 1900° F.

The results of short time aging tests on additional alloys according to the invention, containing beta promoter additions within the limits of their alpha solubilities are shown in the following Table VI. The alloys thus tested were prepared by forging at 1800° F., followed by rolling at 1500° F., to 0.08", then descaled, again rolled at 1400° F. to 0.04", held 15 minutes at 1400° F., furnace-cooled therefrom to 1100° F., held one hour thereat, air cooled thence to room temperature and descaled before testing. In the table, the room temperature mechanical or tensile properties for the alloys are given for the "as rolled and annealed condition," as prepared, supra, in-

cluding minimum bend values, and the minimum bend values are also given for some of the alloys after aging for 48 hours at 750° F.

TABLE VI

Mechanical and aging properties of ternary Ti–Al–*beta–isomorphous alloys*

Composition, Percent (Balance Titanium)	Tensile Properties: p.s.i. × 1,000		Percent Elongation in 1"	Percent Reduction in Area	VHN	Min. Bend Rad. T			
						As Rolled and Annealed		As Aged 48 Hrs. at 750° F.	
	0.2% Offset Yield	Ultimate Strength				L	T	L	T
5Al—1Cb*	89	103	12	40	283				
4Al—2.5Cb	88	97	20	51	309	2.3	2.8	2.1	2.9
5Al—1Ta*	65	79	19	41	300		0.7		
5Al—2.5Ta*	67	80	18	45	276		0.0		
5Al—5Ta*	69	81	18	43	294		1.1		
4Al—5Ta	85	93	23	51	306	2.4	2.4	1.9	1.9
4Al—10Ta	89	98	20	52	317	2.4	2.0	1.8	1.9
2.5Al—1Ag	75	86	22	46	287	1.2	1.6		
2.5Al—2.5Ag	79	91	22	49	289	1.5	1.5		
2.5Al—5Ag	75	89	25	47	287	1.6	1.5		
2.5Al—10Ag	81	88	9	28	317	1.8	1.8		
5Al—1Ag	93	102	19	38	354	1.8	1.8		
5Al—2.5Ag	93	102	22	47	342	1.5	1.5		
5Al—5Ag	93	106	12	31	363	3.4	2.7		
5Al—1 In	82	94	20		321		0.7		
5Al—2.5In	90	100	17		326		1.5		
4Al—2V	101	116	12	35	291	2.4	2.3	2.4	2.4
4Al—2.5V	96	106	19	51	319	2.9	5.7	2.5	2.8
4Al—5Ta—5Cb	121	127	15	44	325	2.7		2.7	
4Al—5Ta—5V	144	145	6	33	351	2.8		3.3	

*Iodide base titanium; balance titanium of commercial purity.

The lower effective limit for the elements having limited solubilities in alpha titanium such as indium, vanadium, columbium, molybdenum, manganese, etc., is about 0.1%, while for those elements having higher alpha solubilities, such as zirconium, hafnium, tantalum, silver, aluminum, tin, antimony, etc., the lower effective limit is about 0.25–0.5%.

Preferred alloys according to the invention are

Ti—(3–6)Al—(4–15)Zr

Ti—(3–6)Al—(4–10)Sn—(5–10)Zr

wherein aluminum and tin are proportioned to provide equivalent aluminum of 6 or under.

The advantages of the present invention are not confined to alloys in accordance therewith having a substantially all-alpha structure, but also apply to such as have imparted thereto a mixed alpha-beta structure due to beta promoter additions in amounts exceeding their alpha solubilities as aforesaid. The effect of such additions is simply to reduce the volume of alpha present in a given total quantity of alloy. Discrete volumes of beta are found, and in these volumes all of the beta stabilizer content beyond that soluble in the alpha is concentrated, and the amount soluble in the alpha remains as described. Hence, obviously, the stability of the remaining alpha is subject to exactly the same conditions as described for the substantially 100% alpha alloy. The most stable of such mixed phase, alpha-beta alloys are those in which the beta promoters added are isomorphous with titanium, such as molybdenum, vanadium, columbium and tantalum, with the sluggishly eutectoid beta promoters next in order such as chromium, manganese and iron, while last in order are the rapidly eutectoid beta promoters tungsten, cobalt, nickel, copper, and particularly silicon and beryllium. The mixed phase alpha-beta alloys will ordinarily not contain more than about 15–18% of such beta promoters, as beyond this they tend to have a substantially all-beta or a mixed beta-eutectoid structure at normal temperatures. For these mixed phase alpha-beta alloys, chromium and manganese should not exceed about 14%, iron about 8%, nickel, cobalt and copper about 5%, and silicon and beryllium about 2%.

Oxidation test data for such alpha-beta alloys in comparison with alpha alloys according to the invention is shown in the following Table VII.

TABLE VII

Oxidation test data for alpha and alpha-beta alloys

[0.075-inch sheet]

Composition, Percent (Balance Titanium)	Temp., F.	Time, hours	Specimen Size, cm.²	Weight Gain, mg.	Weight Gain, mg./cm.²
6Al—4Mo	900	193	11.7	Nil	Nil
6Al—4V	900	193	13.4	Nil	Nil
Unalloyed	900	1,000	85.8	12.0	0.14
5Al—2.5Sn	900	1,000	75.9	4.1	0.05
6Al—4Mo	900	1,000	67.2	3.5	0.05
6Al—4V	900	1,000	74.9	2.4	0.03
Unalloyed	1,000	1,000	82.0	45.7	0.65
5Al—2.5Sn	1,000	1,000	73.2	14.5	0.20
6Al—4Mo	1,000	1,000	69.2	14.7	0.20
6Al—4V	1,000	1,000	68.4	24.2	0.35
6Al—4Mo	1,100	193	9.8	5.6	0.6
6Al—4V	1,100	193	6.9	8.2	1.2
Unalloyed	1,100	1,000	84.5	111.5	1.32
5Al—2.5Sn	1,100	1,000	74.0	41.6	0.56
6Al—4Mo	1,100	1,000	66.3	41.7	0.63
6Al—4V	1,100	1,000	74.9	127.7	1.73
Unalloyed	1,200	1,000	78.9	239.8	3.04
5Al—2.5Sn	1,200	1,000	75.6	108.3	1.43
6Al—4Mo	1,200	1,000	68.4	94.3	1.38
6Al—4V	1,200	1,000	68.7	361.2	5.25

What is claimed is:

1. A titanium base alloy consisting essentially of about: 0.5 to 23% by weight of at least one alpha promoter selected from the group consisting of aluminum, tin, antimony, silver and indium, but not to exceed 7% of aluminum, 3% of indium and 10% of silver, and the maximum total content of the elements of said group being such that the percent of aluminum plus ⅓ times the percents of tin, antimony, silver and indium present, shall not exceed 7%, said alloy being characterized by high strength and ductility and by good stability on aging at 800–1000° C.

2. An alloy consisting essentially of about: 0.5 to 23% by weight of at least one alpha promoter selected from the group consisting of aluminum, tin, antimony,

silver and indium, but not to exceed 7% of aluminum, 3% of indium and 10% of silver, and the maximum total content of the elements of said group being such that the percent of aluminum plus ⅓ times the sum of the percents of tin, antimony, silver and indium present, shall not exceed 7%, said alloy also containing up to 50% of metal of the group zirconium and hafnium, up to 0.5% of metal of the group molybdenum and manganese, up to 3% of metal of the group columbium and vanadium, up to 10% tantalum, and the balance substantially titanium, characterized by high strength and ductility and by high thermal stability.

3. An alloy consisting essentially of about: 0.5 to 23% by weight of at least one alpha promoter selected from the group consisting of aluminum, tin, antimony, silver and indium, but not to exceed 7% of aluminum, 3% of indium and 10% of silver, and the maximum total content of the elements of said group being such that the percent of aluminum plus ⅓ times the sum of the percents of tin, antimony, silver and indium present, shall not exceed 7%, said alloy also containing about 0.25 to 50% of at least one element selected from the group consisting of zirconium, hafnium, columbium, vanadium, tantalum, molybdenum and manganese, but not to exceed 10% of tantalum, 3% of columbium and vanadium and 0.5% of molybdenum and manganese, balance substantially titanium, said alloy being characterized by high strength and ductility and by high thermal stability on aging exposure at 800–1000° F.

4. An alloy consisting essentially of about: 0.5 to 23% by weight of at least one alpha promoter selected from the group consisting of aluminum, tin and antimony, but not to exceed 7% of aluminum, and the maximum total content of the elements of said group being such that the percent of aluminum present plus ⅓ times the sum of the percents of tin and antimony present, shall not exceed 7%, said alloy also containing about 4 to 12% of zirconium, balance substantially titanium, said alloy being characterized by high strength and ductility and by good stability on prolonged aging exposure at about 800–1000° F.

5. An alloy consisting essentially of about: 0.5 to 23% by weight of at least one alpha promoter selected from the group consisting of aluminum, tin and antimony, but not to exceed 7% of aluminum, and the maximum total content of the elements of said group being such that the percent of aluminum present plus ⅓ times the sum of the percents of tin and antimony present, shall not exceed 7%, said alloy also containing about 4 to 12% of hafnium, balance substantially titanium, said alloy being characterized by high strength and ductility and by good stability on prolonged aging exposure at about 800–1000° F.

6. An alloy consisting essentially of about: 0.5 to 23% by weight of at least one alpha promoter selected from the group consisting of aluminum, tin, antimony, silver and indium, but not to exceed 7% of aluminum, 3% of indium, and 10% of silver, and the maximum total content of the alpha promoters of said group being such that the percent of aluminum present plus ⅓ times the sum of the percents of tin, antimony, silver and indium present, shall not exceed 7%, said alloy also containing about 0.1 to 10% of at least one beta promoter selected from the group consisting of tantalum, columbium, vanadium, molybdenum and manganese, but not to exceed 0.5% of molybdenum and manganese, balance substantially titanium, said alloy having a substantially all-alpha microstructure and being characterized by high strength and ductility and by good stability on prolonged aging at 800–1000° F.

7. An alloy consisting essentially of about: 0.5 to 23% by weight of at least one alpha promoter selected from the group consisting of aluminum, tin, antimony, silver and indium, but not to exceed 7% of aluminum, 10% of silver and 3% of indium, and the maximum total content of the elements of said group present being such that the percent of aluminum present plus ⅓ times the sum of the percents of tin, antimony, silver and indium present, shall not exceed 7%, said alloy also containing up to 50% of metal of the group zirconium and hafnium, up to 10% tantalum, up to 3% columbium, up to 0.5% of metal of the group molybdenum and manganese, balance substantially titanium, said alloy having a substantially all-alpha microstructure, and being characterized by a tensile elongation of at least 10% on prolonged aging exposure at 800–1000° F.

8. An alloy consisting essentially of about: 0.5 to 23% by weight of at least one alpha promoter selected from the group consisting of aluminum, tin, antimony, silver and indium, but not to exceed 3% of indium, 7% of aluminum and 10% of silver, and the maximum content of elements of said group present being such that the percent of aluminum present plus ⅓ times the sum of the percents of tin, antimony, silver and indium present shall not exceed 7%, said alloy being characterized by a substantially all-alpha microstructure and by a tensile elongation of at least 10% on prolonged aging exposure at 800–1000° F.

9. An alloy consisting essentially of about: 3 to 6% aluminum, 4 to 12% zirconium, balance substantially titanium, characterized by high strength and ductility and high thermal stability on aging at about 800–1000° F.

10. An alloy consisting essentially of about: 3 to 6% aluminum, 4 to 10% tin, 5 to 12% zirconium and the balance substantially titanium, characterized by high strength and ductility and high thermal stability on aging at about 800–1000° F.

11. An alloy consisting essentially of about: 4 to 6% aluminum, 4 to 12% zirconium, 3 to 6% copper and the balance substantially titanium, characterized by high strength and ductility and high thermal stability on aging at about 800–1000° F.

12. An alloy consisting essentially of about: 0.5 to 23% by weight of at least one alpha promoter selected from the group consisting of aluminum, tin, antimony, silver and indium, but not to exceed 7% of aluminum, 3% of indium, 10% of silver, 20% of tin, and 18% of antimony, and the maximum total content of the elements of said group being such that the percent of aluminum plus ⅓ times the percents of tin, antimony, silver and indium present, shall not exceed 7%, said alloy also containing about 0.5 to 18% of at least one beta promoter, balance substantially titanium, said alloy being characteried by high strength, ductility and thermal stability and by good oxidation resistance at elevated temperatures up to 1800° F.

13. A titanium base alloy consisting essentially of about: 0.5 to 23% by weight of at least one alpha promoter selected from the group consisting of aluminum, tin, antimony, silver and indium, the total content of the elements of said group present being such that the percent of aluminum plus ⅓ the total percent of tin, antimony, silver and indium present is at least 7%, said alloy also containing 0.5 to 3% of metal of the group columbium and vanadium for improving stability of said alloy on aging at about 800 to 1000° F.

14. A titanium base alloy consisting essentially of about: 0.5 to 23% by weight of at least one alpha promoter selected from the group consisting of aluminum, tin, antimony, silver and indium, the total content of the elements of said group present being such that the percent of aluminum plus ⅓ the total percent of tin, antimony, silver and indium present is on the order of 6 to 10%, said alloy also containing 0.5 to 3% of metal of the group columbium and vanadium for improving stability of said alloy on aging at about 800–1000° F.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,892,705 June 30, 1959

Robert I. Jaffee et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 39, for "Ti_2Al" read -- $Ti_3(Al$ --; columns 3 and 4, TABLE I, under the heading "Test Temp., F.", sixth line from the bottom, for "76" read -- 75 --; columns 5 and 6, same TABLE I, continued, under the heading "Composition, Percent (Balance Titanium), third composition from the bottom, for the ingot number "1335" read -- 1435 --; same table, under the heading "Temp. F." line 7, for "700" read -- 800 --; same table, under the heading "Min. Creep Rate per hr.", second line from bottom, for "0.0060" read -- 0.0006 --; column 12, line 72, for "800-1000° C." read -- 800-1000° F. --.

Signed and sealed this 1st day of December 1959.

(SEAL)
Attest:

KARL H. AXLINE
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