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2,892,706

TITANIUM BASE ALLOYS

Robert I. Jaffee, Worthington, and Horace R. Ogden, Columbus, Ohio, assignors, by mesne assignments, to Crucible Steel Company of America, Flemington, N.J., a corporation of New Jersey

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This invention pertains to quaternary and higher order titanium base alloys containing as essential constituents aluminum and chromium together with one or more additional beta promoters, selected more particularly from the beta isomorphous and sluggishly eutectoid beta promoter groups.

A primary object of the invention is to provide titanium base alloys of the character aforesaid, which are characterized by moderately high strength combined with good ductility, especially good bend ductility, and which are further characterized by good thermal stability.

A further object is to provide a titanium base alloy sheet material having the properties aforesaid which is especially adapted for uses such as wing, fuselage and nacelle coverings for airplanes, as compressor casings or housings or as machinery shrouds, and which may also be employed as the structural framework for airplane fuselages and the like.

In our application Serial No. 122,576, filed October 20, 1949, now Patent 2,726,959, we have disclosed a series of ternary Ti—Al—Cr alloys containing about 2 to 7% aluminum with 1 to 15% chromium, which are characterized by good strength and adequate ductility for purposes of fabrication. However, these ternary Ti—Al—Cr alloys have relatively poor thermal stability and for many analyses also relatively poor bend ductility. As an example of this, the Ti—2Al—6Cr ternary alloy has in the annealed condition a minimum bend radius T in excess of 9 in both the longitudinal and transverse directions. On aging 24 hours at 800° F., this alloy becomes quite brittle. As another example, the Ti—5Al—10Cr ternary alloy has, as beta quenched from 1750° F., a minimum bend radius T of 1.2 longitudinal and 0.5 transverse. On aging 16 hours at 850° F., this alloy likewise becomes quite brittle.

Now we have discovered in accordance with the present invention, that the thermal stability of these Ti—Al—Cr base alloys is greatly improved by additions thereto of one or more beta promoting elements, in addition to the chromium present, and selected more particularly from the beta isomorphous and sluggishly eutectoid beta promoter groups. Although all of the beta isomorphous promoters, namely, molybdenum, vanadium, columbium and tantalum, improve thermal stability of these Ti—Al—Cr alloys, best results are obtained with additions of vanadium and/or molybdenum. Of the sluggishly eutectoid beta promoters, other than chromium, namely, manganese, iron and tungsten, additions of manganese and/or iron give the best results, with tungsten somewhat less effective. Excellent results are also secured with combinations of the beta isomorphous and sluggishly eutectoid beta promoters, such for example, as vanadium or molybdenum with manganese or iron. The rapidly eutectoid beta promoters cobalt and nickel when present in small amounts, as noted below, also afford some improvement, but not to the extent of the beta promoters above noted.

Additions of these beta promoters to the Ti—Al—Cr

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base alloys of our aforesaid parent application, in general also improve the ductility, both the tensile ductility as well as the bend ductility, and especially the latter, without impairment of strength.

As illustrative of the improvements thus effected by such additions, if in the Ti—2Al—6Cr ternary alloy aforesaid, there is substituted 3% of manganese for a corresponding amount of chromium, the resulting alloy has in the as annealed condition a minimum bend T of 1.0 longitudinal and 3.6 transverse. After aging 24 hours at 800° F., the minimum bend T is 1.1 longitudinal and 2.3 transverse, thus clearly evidencing the thermal stability and excellent bend ductility of the alloy resulting from the manganese substitution. Similarly if 2% molybdenum and 2% manganese is substituted for a like amount of the chromium in the aforesaid Ti—2Al—6Cr alloy, the resulting quaternary alloy has in the as annealed condition a minimum bend T of 1.1 longitudinal and 3.0 transverse. After aging as aforesaid, these bend values become 1.6 longitudinal and 2.5 transverse, again showing the thermally stabilizing effect of the substituted metal, as well as the excellent bend ductility obtained both in the as annealed as well as in the as aged condition.

The improvement in ductility from such additions is not only evident from the bend ductility values aforesaid, but is also reflected in the ductility as measured by tensile elongation. Thus, whereas the Ti—2Al—6Cr alloy has as annealed a tensile elongation of 6%, that for the Ti—2Al—3Cr—3Mn alloy is 13% and for the Ti—2Al—2Cr—2Mn—2Mo alloy is also 13%. Accordingly, the substitution of manganese or molybdenum for half of the chromium in the aforesaid Ti—Al—Cr base alloy has improved the tensile ductility two- to three-fold, and has improved the bend ductility to a far greater extent.

This increase in ductility is moreover secured without impairment of the tensile strength of these alloys, which is in fact often increased by the beta promoter additions to the Ti—Al—Cr base. Thus for the Ti—2Al—6Cr alloy as annealed, the ultimate strength is 122,000 p.s.i. as against 141,000 p.s.i. for the Ti—2Al—3Cr—3Mn alloy and 139,000 p.s.i. for the Ti—2Al—2Cr—2Mn—2Mo alloy.

As above noted, although the Ti—5Al—10Cr ternary alloy has good bend ductility as beta quenched from 1750° F., nevertheless on aging at 850° F., this alloy becomes quite brittle. As compared to this, if there is added to this base alloy approximately 12% vanadium, the resulting quaternary alloy has as annealed, a minimum bend T of 0 longitudinal and 0.7 transverse. On aging 24 hours at 800° F., these bend values become 1.5 longitudinal and 2.7 transverse, as compared to the entirely brittle metal obtained on correspondingly aging the ternary alloy.

In the following Table I, there is shown the room temperature mechanical properties, in the as rolled and annealed condition of various quaternary and higher order alloys according to the invention, as compared to typical Ti—Al—Cr ternary alloys; while the following Table II shows the effect of aging on bend ductility of various of the alloys shown in Table I.

The test results given in these tables as well as those above discussed, are based on alloys made from titanium metal of commercial purity as produced by the magnesium reduction of titanium tetrachloride. To the titanium sponge thus obtained were added alloying metals of highest purity, and the resulting alloy produced by arc melting in an inert or argon atmosphere in a cold mold or water-cooled copper crucible. The ingots thus produced were forged into billets at about 1800° F., rolled at about 1400° F., into sheet of about 0.04" gauge, and thereupon annealed at 1400° F., and the specimens thus

produced, tested with results as set forth in Tables I and II.

In our U.S. Patent 2,596,485, granted May 13, 1952, we have disclosed a series of strong, ductile and thermally

TABLE I
Room temperature mechanical properties in the annealed condition of the alloys

Composition, Percent (Balance Titanium)			Tensile Properties: p.s.i. × 1,000		Percent Elongation in 1"	Percent Reduction in Area	Vickers Hardness	Minimum Bend T	
Al	Cr	Other	0.2% Off-set Yield	Ultimate Strength				L	T
---	---	---	48	71	21	51	187	0.8	0.8
*2	6	---	108	124	6	13	315	9.4	>9.0
*4	2	---	109	122	9	28	326	3.6	4.0
4	5	---	140	143	5	16	336	5.0	6.5
4	2.5	V5	138	146	9	28	338	2.4	8
4	5	5V	130	138	9	20	297	2.0	---
3.6	8	11.7V	131	135	21	35	---	0	0.3
*4.7	4	12.4V, 8 Mn	139	142	13	38	---	0.0	1.0
*5.4	10.8	12.3V	134	139	13	32	---	0	0.7
4	7.5	7.5Mo	138	141	8	36	306	0	0
4	2.5	5Ta	123	129	7	29	349	7.5	7.8
*2	3	3Mn	129	141	13	29	292	1.0	3.6
4	2.5	2.5Mn	138	144	6	33	358	1.8	1.8
4	7.5	4Mn	138	142	11	38	319	0	0
*2	2	2Mn, 2Mo	128	139	13	31	293	1.1	3.0
5	1.25	1.25Fe	111	131	11	32	336	1.2	---
5	1.25	1.25Fe, 0.25C	140	150	6	26	375	1.5	---
4	2.5	1.5Fe	139	146	4	22	346	1.8	8
4	7.5	3Fe	134	138	10	40	320	0	0
4	2.5	2.5W	136	140	13	42	351	2.8	3.7
4	2.5	2Co	135	145	9	35	353	2.6	7.8
4	2.5	2Ni	111	126	1	6	320	7.5	8
4	2.5	5Cb	139	145	11	37	355	2.4	3.6

*Average of four tests.

TABLE II
Effect of aging on bend ductility

Composition, percent (Balance Titanium)			As Annealed		After Aging 24 Hours at 800° F., Except as Indicated	
Al	Cr	Other	L	T	L	T
2	6	---	9.4	>9.0	Brittle	
4	2	---	3.6	4.0	4.9	4.2
5	10	---	*1.2	0.5	Brittle	
2	3	3Mn	1.0	3.6	1.1	2.3
2	3	2Mn, 2Mo	1.1	3.0	1.6	2.5
4	7.5	7.5Mo	0.0	0.0	>8	>7
3.6	8	11.7V	0.0	0.3	*1.2	1.8
5.4	10.8	12.3V	0.0	0.7	*1.5	2.7
4.7	4	12.4V, 8Mn	0.0	1.0	*1.3	2.3

a Quenched from 950° C.
b Aged 16 Hrs. at 450° C.
c Aged at 750° F.

Referring to Table I, it will be seen that the quaternary and higher order alloys of the invention in general possess superior ductility, both in tensile elongation and in bend, as compared to the ternary Ti—Al—Cr alloys. This is shown to be particularly true for additions to the Ti—Al—Cr base alloys of such isomorphous beta promoters as vanadium and molybdenum and such sluggishly eutectoid beta promoters as manganese and iron. By such additions bend values on the order of 0 to 2 or 3T are easily obtainable, with corresponding minimum tensile elongations on the order of about 10%. Furthermore, the improvement in ductility is in general secured at no sacrifice in tensile strength. To the contrary, the tensile strength is in general improved somewhat as compared to the corresponding ternary alloy.

Referring now to Table II, it will be seen that aging in general has quite an embrittling effect on the ternary Ti—Al—Cr alloys, whereas the quaternary and higher order alloys of this invention are shown to be quite stable thermally, as evidenced by the slight variation in bend ductility as a result of the aging as compared to the non-aged or as annealed condition of the alloy. This is particularly true for the alloys containing relatively large amounts of the isomorphous beta promoters like molybdenum and vanadium.

stable quaternary Ti—Al—Cr—Mo alloys containing 2 to 5% aluminum together with 1 to 6% each of chromium and molybdenum. This patent states, however, that quaternary Ti—Al—Cr—Mo alloys containing larger amounts of chromium and molybdenum are brittle and particularly so after aging. These conclusions were based on our earliest experiments with these Ti—Al—Cr—Mo alloys. As a result of our further investigations, however, we have now found that such alloys not only possess good strength and ductility but in addition are not unduly embrittled on aging. This is shown by the test results for the Ti—4Al—7.5Cr—7.5Mo alloys of Tables I and II. As there shown, this alloy has in the as annealed condition a tensile strength of 141,000 p.s.i., a tensile elongation of 8% and a minimum bend T of 0.0 both longitudinal and transverse. On ageing 24 hours at 800° F., the bend ductility is increased to something over 8T, which is not excessive, since these alloys are usable in sheet form with bend ductilities up to 20T as noted below.

Our experiments subsequent to those forming the basis of our patent have shown, as attested by the above data, that where the isomorphous beta promoters like molybdenum or vanadium are present in relatively large amount, relatively large amounts of chromium may be present, consistent with the attainment of the combination of good strength, ductility and thermal stability. Thus the alloys of the present invention which are high in chromium plus isomorphous beta promoters like molybdenum and vanadium possess a combination of desirable properties not previously known or suspected.

For the quaternary and higher order alloys of this invention, aluminum may be present over the broad range of 0.5 to 8% together with chromium over the range of 0.5 to 20%, the chromium in general being on the high side when aluminum is present on the low side of its range and vice versa. Preferred ranges are about 2 to 7% aluminum with about 1 to 15% chromium.

The beta isomorphous promoters molybdenum, vanadium, columbium and tantalum may be added over the range of 0.5 to 40%, individually or in total amount. Of the sluggishly eutectoid beta promoters, manganese is effective up to about 10% and iron and/or tungsten

up to about 7%. The rapidly eutectoid beta promoters nickel and cobalt should not be present in excess of 5% individually or in total amount. The lower effective limit for all of these eutectoid beta promoters is about 0.5%.

The interstitials carbon, oxygen and nitrogen may be present in the quaternary and higher order alloys of the invention to about the same extent as in the corresponding ternary alloys. That is to say, carbon may usefully be added up to about 0.3%, oxygen up to about 0.25% and nitrogen up to about 0.15%, the total carbon, oxygen and nitrogen, however, not to exceed about 0.5%. Within these limits these interstitial additions strengthen the alloy without unduly embrittling the same.

The vanadium-containing alloys of the invention containing about 5 to 15% vanadium, in which chromium is substituted for about one-half the vanadium, exhibit the further desirable property of being very responsive to heat treatment. Very high strengths with useful ductility can be secured for these alloys by quenching and aging. This is shown, for example, by the data for the Ti-4Al-5Cr-5V alloy as given in the following Table III:

TABLE III

Properties of a Ti-4Al-5Cr-5V alloy

[This alloy was forged at 1800° F., rolled at 1500° F. to 0.1-inch sheet, rolled at 1400° F. to 0.04-inch sheet, then given treatments as indicated below.]

Aging Treatment		0.2% Offset Yield Strength, 1,000 p.s.i.	Ultimate Strength, 1,000 p.s.i.	Elong., Percent in 1"	Red. in Area, Percent	VHN	MBR, T Long.
Time, hr.	Temp., C.						
INITIAL CONDITION: 4 HOURS AT 750° C. AND WATER QUENCHED							
		130	138	9	20	297	2.0
1/4-----	400	188	190	3	16	456	Br
1-----	500	189	200	5	14	470	4.3
4-----	500	197	208	7	9	386	3.0
16-----	500	190	202	5	13	454	9.9
64-----	500	191	195	2	3	416	Br
INITIAL CONDITION: 4 HOURS AT 700° C. AND WATER QUENCHED							
		135	140	11	22	322	0.4
1/4-----	400	144	148	12	20	325	0.4
1-----	500	165	176	10	18	382	1.6
16-----	500	161	168	7	18	378	1.5

It will be seen from the foregoing data that by quenching from the higher temperature (750° C.) a greater aging response is obtained because there is more unstable beta phase present than when the alloy is quenched from the lower temperature (700° C.). Both of these quenching temperatures are in the alpha/beta field for this alloy. Thus the properties of the alloy can be controlled by altering both the solution annealing (quenching) temperature, and the aging treatment.

The alloys of the present invention may be fabricated in massive form, as by forging, where the tensile elongations are upwards of 1 or 2%. They are useful in sheet form with minimum bend values up to about 20T.

This application is a continuation-in-part of our copending applications Serial No. 122,576, filed October 20, 1949, now Patent 2,726,954; Serial No. 305,284, filed August 19, 1952, now Patent 2,798,806; Serial No. 479,242, filed December 31, 1954, now Patent 2,754,204; Serial No. 400,730, filed December 28, 1953, now

abandoned; and Serial No. 392,052, filed November 13, 1953, now abandoned.

What is claimed is:

1. A titanium base alloy consisting essentially of about: 0.5 to 8% aluminum, 0.5 to 20% chromium and about 0.5 to 10% manganese, balance substantially titanium, said alloy being characterized by good bend ductility and thermal stability.
2. A titanium base alloy consisting essentially of about: 0.5 to 8% aluminum, 0.5 to 20% chromium and about 0.5 to 7% tungsten, balance substantially titanium, said alloy being characterized by good bend ductility and thermal stability.
3. A titanium-base alloy consisting essentially of about: 0.5 to 8% aluminum, 0.5 to 20% chromium and about 0.5 to 5% cobalt, balance substantially titanium, said alloy being characterized by good bend ductility and thermal stability.
4. A titanium-base alloy consisting essentially of about: 0.5 to 8% aluminum, 0.5 to 20% chromium and about 0.5 to 5% nickel, balance substantially titanium, said alloy being characterized by good bend ductility and thermal stability.
5. A titanium base alloy consisting essentially of about: 0.5 to 8% aluminum, 0.5 to 20% chromium, 0.5 to 5% columbium, balance substantially titanium, said alloy being characterized by good bend ductility and thermal stability.
6. A titanium base alloy consisting essentially of about: 0.5 to 8% aluminum, 0.5 to 20% chromium, 0.5 to 10% of at least one element selected from the group consisting of tantalum, columbium, manganese, tungsten, cobalt and nickel, balance substantially titanium, characterized by high tensile strength, good ductility and thermal stability.

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