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THERMALLY STABLE BETA ALLOYS OF TITANIUM-TIN ALLOYS

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This invention pertains to titanium base alloys containing one or more beta promoters or stabilizers, together with tin in amount such as to function as a retardant of phase change or eutectoid decomposition during aging of the alloy.

As is known, the metal titanium in the pure state, is capable of existing in either of two allotropic forms. Below a temperature of about 885° C. or 1625° F., it assumes a close-packed hexagonal microstructure known as the alpha phase, while at this temperature and above it assumes a body-centered cubic structure known as the beta phase.

Certain substitutional alloying additions to the titanium base metal, among which may be mentioned aluminum, indium, antimony, bismuth, lead and silver, as well as the interstitials carbon, oxygen and nitrogen, tend to stabilize the alpha phase. The substitutional alloying addition tin, likewise in general functions as an alpha stabilizer, and heretofore has been exclusively regarded as such.

Other substitutional alloying elements, when added in progressively increasing quantities, stabilize the beta phase at progressively lower temperatures, until a mixed alpha-beta or stable all-beta microstructure is obtained at normal or atmospheric temperatures, or the beta phase undergoes a eutectoid reaction, depending on the character and amount of the beta stabilizers added.

Speaking in broadest terms, the beta stabilizers are Mn, Mo, Cr, Fe, Cu, V, Zr, W, Nb, Ta, Co and Ni. Silicon and beryllium may also be considered as beta stabilizing elements, but their solubilities in titanium are relatively small, so that it is equally proper to consider them as compound-forming elements. Within this broad category, however, only certain of the elements mentioned are suitable for producing mixed-phase alpha-beta alloys, or stable beta alloys. These are the elements which have beta-isomorphous diagrams, or which have beta-eutectoid diagrams such that the decomposition of the beta phase into eutectoid is so sluggish that the alloys behave like those in a beta-isomorphous system. The beta stabilizing elements of this type are Mn, Mo, Cr, Fe, V, Nb, W and Ta.

Zirconium is a beta promoter or stabilizer in the sense that the lowest temperature at which the alloy thereof with titanium is entirely beta, becomes progressively lower with increasing amounts of zirconium, until a temperature is reached at which this so-called beta transus temperature starts to increase again with increasing additions of zirconium. Additions of up to 20% zirconium have proved effective in this respect. While zirconium thus lowers the transformation temperature of titanium, the alloys eventually revert to the alpha phase at lower temperatures unless other beta promoters are present.

The use of copper alone as an alloying addition to titanium, does not fit into the last-mentioned group of beta stabilizing elements, because the beta phase stabi-

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lized by copper always decomposes into pro-eutectoid and eutectoid products, and the same is generally true with respect to cobalt, nickel, silicon and beryllium, above listed under the broad category of beta stabilizers. Copper, however, is a useful addition when present as a minor alloying element, for example, up to a few percent, in alloys containing larger amounts of other beta stabilizing elements, within the narrow group of elements last mentioned above since, in these low concentrations and in the presence of such other beta stabilizing elements, the tendency of copper to decompose into eutectoid products is minimized or entirely eliminated.

Substantially pure and ductile metallic titanium may be produced at considerable expense by the so-called "iodide" process described in U. S. Patent 1,671,213 to Van Arkel; while ductile titanium of commercial purity can be produced more cheaply by the magnesium reduction of titanium tetrachloride by the process described in U. S. Patent 2,205,854 to Kroll. Both procedures, particularly the latter, result in some contamination of the titanium metal with one or more of the interstitials, carbon, oxygen and nitrogen. But since, as noted above, these are all alpha promoting or stabilizing elements, the resultant titanium metal obtained, has at room temperatures a single phase, all-alpha microstructure.

The all-alpha, all-beta and mixed alpha-beta alloys of titanium have their respective advantages and disadvantages. Generally speaking, the alpha alloys provide good all around performance, having good weldability, and being strong and resistant to oxidation, both cold and hot, but are somewhat inferior as to ductility. The all-beta alloys, on the other hand, have excellent bendability and ductility, are strong both hot and cold, but are somewhat vulnerable to atmospheric contamination, particularly at elevated temperatures. The mixed alpha-beta alloys provide a compromise performance as between all-alpha and all-beta alloys, being strong when cold and warm, but weak when hot, while possessing good bendability and ductility, with a moderate degree of resistance to atmospheric contamination.

Investigations have shown that there are relatively few all-beta titanium base alloys which remain stable on aging at elevated temperatures. The vast majority would more correctly be classified as unstable beta alloys, in that they have an all-beta microstructure on rapid cooling or quenching from the beta field, but which on subsequent aging or hot working, at temperatures below 1625° F. or 885° C., transform in greater or lesser degree into the alpha phase or into eutectoid decomposition products or into both. This phase transformation tends to embrittle the alloy, so much so for many analyses as to entirely destroy ductility for fabrication purposes.

Now I have discovered in accordance with the present invention that this phase transformation and accompanying embrittlement of many such beta alloys is greatly minimized by the addition of tin in amounts critically related to the aggregate content of the beta promoting elements present in the alloy.

Although, as above stated, tin has heretofore been regarded exclusively as an alpha stabilizing element, I have discovered in accordance with my invention, that curiously enough, when added in appropriate amounts to beta alloys of the character aforesaid, tin apparently functions as a beta stabilizing element, at least to the extent of greatly retarding or eliminating the conversion of the beta phase to alpha and/or eutectoid decomposition products as a result of aging by or during exposure to moderately elevated temperatures in use, as for example, in some of the more important applications, such as in jet shrouds, high performance aircraft skins, etc.

I have determined experimentally, as evidenced by the

test results presented below, that in general the thermal stability of beta alloys of titanium is markedly improved by additions of tin in amounts ranging from about 3 to 7%, with an optimum effect occurring in general at about 5%. This represents the preferred range of the tin additions for most effective thermal stabilizing action, and particularly as applied to titanium base alloys containing an aggregate of not over about 20%, and preferably about 12 to 17%, of beta promoting or beta transus temperature lowering elements.

For certain beta alloys of titanium, tin additions as low as about 2%, and as high as about 10% are found to impart noticeable or substantial thermal stabilization. Within this broad range smaller tin additions are most effective in the alloys containing higher aggregate contents of beta promoters and vice versa. Thus, with upwards of 20% in aggregate of beta transus temperature lowering

elements present in the alloy, something under 5% tin and ranging down to about 2% is most effective. On the other hand, with an aggregate content of something on the order of 10% beta transus temperature lowering elements present, as much as 10% or more of tin may be required for most effective thermal stabilization. On the other hand, for alloys containing an aggregate of beta promoters within the preferred range of about 12 to 17%, little benefit is gained from tin additions as low as 2%, while additions as high as 10%, appear in general to be detrimental.

In the test results set forth in Table I below, in support of the above, two criteria for thermal stability have been employed, (a) hardness changes, and (b) bend ductility changes, with aging. With reference to these data, increase in hardness without drastic loss of bend ductility, is considered a promising indication for the heat

TABLE I

Effect of tin additions on thermal stability of beta titanium base alloys

Composition, Percent (Balance Titanium)		A As Rolled and Annealed		B 24 Hrs. at 750° F.		C 100 Hrs. at 750° F.		D 100 Hrs. at 500° F.	
Sn	Other	Bend T	Ra	Bend T	Ra	Bend T	Ra	Bend T	Ra
0.	12Mn	2.1	67	¹ B	73	B	7	10	---
5.	12Mn	2.4	64	3.6	66	5.2	60	1.4	---
0.	12Mo	3.5	56	---	---	5.2	65	4.4	61
5.	12Mo	3.6	62	---	---	---	---	3.9	56
4.	3.5Mo	1	64	2.3	---	B	72.5	---	---
0.	12Fe	¹ B	69	B	---	B	74	B	70
5.	12Fe	B	71	B	---	B	72	B	70
0.	12Cr	B	75	B	---	B	75	B	76
5.	12Cr	1	64	---	75	B	72	B	72
10.	10Zr	4.1	63	5.2	64	5.4	64	4.2	63
4.5.	9V	4.6	63	---	---	4.7	63	5.5	64
6.5.	9V	5.2	63	---	---	3.8	65	4.0	67
2.	12V	4.9	65	---	---	3.2	65	6.1	67
4.5.	13.5V	3.5	63	3.9	---	3.9	66	0.4	69
0.	7Mn, 8Cr	1	64	2.8	67	B	---	B	---
5.	7Mn, 8Cr	1.5	65	3	66	3.9	---	3.7	---
10.	7Mn, 8Cr	B	68	B	---	B	---	B	---
0.	9Mn, 6Cr, 0.2O	2.6	66	---	---	B	73	5.6	70
5.	9Mn, 6Cr, 0.2O	4.6	68	---	---	6.3	67	5.6	68
0.	9Mn, 6Cr	1.8	67	6.4	68	B	73	7.1	69
5.	9Mn, 6Cr	1.1	67	3.3	67	6.2	68	1.1	66
10.	9Mn, 6Cr	B	71	B	---	B	70	B	70
0.	5Mn, 10Cr	1.5	64	---	67	B	74	B	73
5.	5Mn, 10Cr	2.4	65	---	65	B	69	5.7	65
0.	6Mn, 9Cr	1	65	8.1	71	B	73	B	71
5.	6Mn, 9Cr	1	65	1.3	66	4.9	68	0.5	66
0.	7Mn, 7Mo	B	72	B	74	B	71	B	73
5.	7Mn, 7Mo	1.7	64	---	67	B	71	1.2	66
0.	10Mn, 5Mo	1.3	61	---	67	B	72	3.6	64
5.	10Mn, 5Mo	1	63	---	64	5.5	67	2.6	63
10.	10 Mn, 5Mo	B	68	B	---	7.3	69	B	70
0.	6.5Cr, 6Mo	6.4	66	---	---	7.6	69	4.7	67
0.	6.5Cr, 7Mo	6.4	65	---	---	5.5	67	5.8	68
5.	10Cr, 5Mo	B	73	B	75	B	---	B	---
0.	10Cr, 5Mo	2.2	64	---	67	B	71	7.4	69
0.	7Cr, 7Mo	6.4	67	10	69	7	69	10	71
5.	7Cr, 7Mo	3.6	61	6.8	66	10	70	10	68
0.	7Mo, 8Fe	3.9	67	---	68	B	72	7.3	69
5.	7Mo, 8Fe	2.4	66	---	66	B	72	2.8	67
0.	8Mn, 7Fe	B	68	B	68	B	---	B	---
5.	8Mn, 7Fe	B	70	B	70	B	---	B	---
0.	8Cr, 7Fe	2	67	4	68	B	71	4.5	67
0.	10Cr, 5Fe	1	67	5	68	B	---	B	---
5.	10Cr, 5Fe	4.7	68	7.8	68	---	68.5	3.4	---
0.	7Mn, 4Cr, 4Mo	3.1	63	---	69	B	72	8	70
5.	7Mn, 4Cr, 4Mo	1	64	1	65	2.4	66	0.9	65
0.	7Mn, 4Cr, 4Mo, 0.2O	6.8	66	---	75	7.4	69	7	72
5.	7Mn, 4Cr, 4Mo, 0.2O	5.7	67	---	67	5.5	67	6	68
5.	10Mn, 5Cr, 5Mo	4.2	68	4	67	8.3	68	4	67
4.	6Mn, 3Cr, 3.3Mo	1.1	---	7.8	71	7.0	---	8.6	---
0.	5Cr, 5Mo, 5Fe	3.5	67	---	69	B	74	7.6	71
5.	5Cr, 5Mo, 5Fe	6	67	---	68	6.6	65	5.7	68
0.	5Mn, 5Cr, 5Fe	3	67	7	67	---	---	7	---
5.	5Mn, 5Cr, 5Fe	2.5	68	B	68	B	---	6	---
4.	3.3 each of Mn, Cr, Mo, Fe	1	64	2.8	---	---	---	2.4	65
0.	4 each of Mn, Cr, Mo, Fe	2.8	66	---	66	B	71	1.7	67
5.	4 each of Mn, Cr, Mo, Fe	2.2	67	---	67	6.6	68	3.7	68
0.	12Mn, 1Cu	1.6	65	8	68	B	---	B	---
5.	12Mn, 1Cu	1	65	4.1	66	7	---	2.3	---
5.	12Mn, 2Mo, 1Cu	2	62	---	65	7.3	69	2.9	64
10.	12Mn, 2Mo, 1Cu	B	69	B	---	B	69	B	71
0.	7Mn, 5Cr, 7Zr	2.5	65	---	73	B	74	B	73
5.	7Mn, 5Cr, 7Zr	1.8	68	---	67	7.1	70	4.1	67
0.	7V, 5Cr, 5Mn	3.6	67	---	---	B	72	4.7	68
4.	5.5V, 5Cr, 6Mn	4.0	66	---	---	B	71	3.5	68

¹ B = completely brittle.

² B in column A is, of course, B in all columns.

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treatable beta alloys. It has been found, however, that any hardness increase by aging alone to Rockwell "A" 70 or above, is almost invariably associated with more or less complete embrittlement. In Table I, the test data of column A gives the bend ductility and Rockwell "A" hardness, of each alloy of the analysis shown, in the condition resulting from rolling at 1400° F. to an intermediate gauge followed by cleaning and further rolling at 1300° F. final gauge, and thereupon holding at 1300° F. for one-half hour and furnace cooling to 1100° F., and finally air cooling to room temperature. Column B gives the bend ductility and Rockwell "A" hardness for the specimens as prepared under A, and thereupon aged for 24 hours at 750° F.; while columns C and D give data corresponding to column B, except that the aging is carried out for 100 hours at 750° F. for column C and for 100 hours at 500° F. for column D.

Referring to the data of Table I, it will be observed that, in general, the beta alloys which are embrittled and unduly hardened on aging in the absence of tin, are converted into thermally stable alloys by appropriate tin additions and retain adequate ductility and low hardness under the various aging conditions set forth. The thermal stabilizing action of the tin varies somewhat with the specific beta promoting elements present. With reference to the binary alloys shown, tin is quite effective in imparting thermal stability to those in which the beta promoting element comprises manganese, and possibly zirconium or vanadium, but offers no material improvement as regards those in which the beta promoter is molybdenum, iron or chromium. On the other hand, it is quite generally true that the tin addition offers a great improvement with respect to practically all of the ternary and quaternary alloys such as the manganese-chromium, manganese-molybdenum and chromium-molybdenum ternaries. Also improvement is shown in certain of the ternaries containing iron, particularly where the iron is present in amounts not exceeding about 5%. All of the quaternary alloys are materially improved as to thermal stability by the tin additions, the majority of those generally being embrittled on aging in the absence of tin, but in maintaining adequate ductility with low hardness under the most severe aging conditions when tin is present in appropriate amounts.

From this generalization may be drawn that a multiplicity of beta stabilizers in the alloy along with tin appears to be generally advantageous, provided that no one of the beta promoters is present in excessive or preponderant amount as compared to the others, except possibly manganese.

The test results of Table I further establish that the alloys according to the invention which are found to be most stable thermally are those containing about 15% in aggregate of a multiplicity of beta transus temperature lowering elements, together with about 5% tin.

Since the elevated temperature range within which titanium possesses advantages in use over other materials, is about 400-800° F., the aging tests of Table I were carried out within this range.

The alloys of the invention may be made by melt casting in a cold mold employing an electric arc and an inert atmosphere, or may be produced in other ways in which the alloy is rendered molten before casting.

My experiments on high beta, titanium base alloys, indicate that while alpha separation resulting from over-aging does not necessarily impair ductility seriously, the same is not true with respect to eutectoid decomposition, which results only in increasing embrittlement. Hence, in seeking a stable beta alloy, the advantage gained in beta transus temperature lowering by adding more and more of the beta stabilizers, is offset by the increasing tendency toward eutectoid decomposition. In this connection, the non-eutectoid beta stabilizers, such as V, Cb, Ta and Mo are

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either too expensive, rare or heavy to be employed alone. For this reason, tin is a particularly valuable addition to the beta alloys of titanium. As shown above, tin is not a beta stabilizer in the sense that V, Cb, Ta, etc., are. The latter lower the equilibrium beta transus temperature, while tin does not. As stated, tin has heretofore been considered as an alpha stabilizer. But with respect to the alloys of the present invention, although tin confers sluggishness to the beta decomposition, it does not, itself, form a eutectoid with titanium. Hence the effect of adding tin to the alloys of the invention is that of adding a true beta transus temperature lowering element, while at the same time suppressing eutectoid decomposition. In this respect it stands in marked contrast to the beta transus temperature lowering elements, since the latter other than the expensive, rare or heavy ones, increase the tendency to eutectoid decomposition.

It is thus shown that tin, normally an alpha stabilizer, nevertheless renders beta alloys sluggish in decomposition. Also, that the addition of tin provides effectively stable beta alloys at lower aggregate contents of the beta promoters which produce eutectoid decomposition, than is obtainable in the absence of tin. The tin additions also effectively thermally stabilize many of the beta analyses which would otherwise be unstable on aging.

It is to be understood that the beta alloys in accordance with the invention may also contain one or more of the alpha promoters above listed, provided they are not present in sufficient amount to destroy the beta characteristics of the alloy.

In the appended claims, by the expression "beta promoting elements" is meant an element of the group molybdenum, vanadium, columbium, tantalum, zirconium, chromium, manganese, iron, tungsten, cobalt, nickel, copper, silicon and beryllium.

I claim:

1. A titanium-base alloy consisting essentially of: about 10 to 20% of at least one beta-promoting element, about 2 to 10% tin, and the balance substantially titanium, characterized by high thermal stability and retention of ductility on aging in the temperature range of about 400 to 800° F.

2. A titanium-base alloy consisting essentially of: about 10 to 20% of at least two beta-promoting elements, about 2 to 10% tin, and the balance substantially titanium, characterized by high thermal stability and retention of ductility on aging in the temperature range of about 400 to 800° F.

3. A titanium-base alloy consisting essentially of: about 10 to 20% of at least three beta-promoting elements, about 2 to 10% tin, and the balance substantially titanium, characterized by high thermal stability and retention of ductility on aging in the temperature range of about 400 to 800° F.

4. A titanium-base alloy consisting essentially of: about 10 to 20% of at least one beta-promoting element selected from the group consisting of molybdenum, vanadium, columbium, tantalum, zirconium, chromium, manganese, iron, tungsten and copper, about 2 to 10% tin, and the balance substantially titanium, characterized by high thermal stability and retention of ductility on aging in the temperature range of about 400 to 800° F.

5. A titanium-base alloy consisting essentially of: about 10 to 20% of at least two beta-promoting elements selected from the group consisting of molybdenum, vanadium, columbium, tantalum, zirconium, chromium, manganese, iron, tungsten and copper, about 2 to 10% tin, and the balance substantially titanium, characterized by high thermal stability and retention of ductility on aging in the temperature range of about 400 to 800° F.

6. A titanium-base alloy consisting essentially of: about 10 to 20% of at least three beta-promoting elements, selected from the group consisting of molybdenum, columbium, tantalum, zirconium, chromium, man-

ganese, iron, tungsten and copper, about 2 to 10% tin, and the balance substantially titanium, characterized by high thermal stability and retention of ductility on aging in the temperature range of about 400 to 800° F.

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