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TITANIUM BASE ALLOY

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ABSTRACT OF THE DISCLOSURE

Titanium base alloy consisting essentially of about 2.5-7.5% zirconium, 2.5-10% molybdenum, up to 0.5% and preferably 0.25-0.5% beryllium, up to 0.35% in total amount of carbon, oxygen and nitrogen, balance substantially titanium, characterized in being age hardenable and by high resistance to stress corrosion cracking in a chloride environment at elevated temperature.

This invention relates to a strong and ductile titanium base alloy characterized by immunity to stress corrosion cracking in a chloride environment at elevated temperature, and more particularly to an alloy so characterized containing about 2.5% to 7.5% zirconium and 2.5% to 10% molybdenum as essential constituents.

Stress corrosion cracking occurs in titanium base alloys when exposed to temperatures above about 500° F. under stress and in contact with a halide salt or atmosphere. Typically, it occurs when such alloys are in a chloride environment, as in contact with sodium chloride. Stress corrosion cracking manifests itself as the formation of cracks or fissures on the surface of the alloy at the grain boundaries. These cracks become progressively larger and deeper with increased exposure time. When the cracking becomes severe enough to destroy the structural integrity of the material, it fails catastrophically. Generally speaking, titanium base alloys containing more than 1% of alloy additions that are at present commercially sold and used are susceptible, to a more or less extent, to stress corrosion cracking. Certain titanium alloys containing only up to a few tenths of one percent of a metal such as palladium are corrosion resistant and immune to stress corrosion cracking. Such alloys, however, show mechanical properties similar to commercially pure titanium, including a similar low strength level.

Titanium base alloys comprise compositions containing titanium as the predominant element together with various alloying elements, including those that stabilize alpha phase titanium, such as aluminum, tin, antimony, indium, etc., and those that stabilize beta phase titanium, such as vanadium, tantalum, columbium, chromium, molybdenum, iron, tungsten, cobalt, nickel, manganese and copper. Alloys composed essentially of titanium and alpha stabilizing alloying metals will consist substantially of alpha phase titanium, while those containing appreciable amounts of beta stabilizers will contain some proportion of beta phase titanium at room temperature. Generally speaking, titanium base alloys containing either or both types of stabilizer will be stronger than pure titanium, their precise properties depending on the amounts and types of alloying elements present. A number of titanium base alloys have found wide commercial acceptance for use in fabrication of structures requiring lightness and strength, for example, airframe and jet engine parts and missile components. Typical of such alloys are those containing 6% Al-4% V, 8% Al-1% Mo-1% V, and 5% Al-2.5% Sn. A representative commercial alloy of the so-called all-beta type contains 13% V-11% Cr-3% Al.

Commercially pure titanium can be produced to possess mechanical properties within a fairly wide range, depending principally on the content of the interstitials oxygen and nitrogen. Ultimate tensile strengths of up to 80,000 to 100,000 p.s.i. may be obtained in commercially pure titanium containing a relatively large proportion of the interstitials oxygen and nitrogen and also carbon, but such strengths are obtained at the expense of some loss in ductility. Commercially pure titanium is used for structural purposes where the higher strengths of titanium base alloys are not required and also in chemical plant construction because of the advantage of its high resistance to corrosion.

The present commercial titanium base alloys in spite of their excellent strengths, which in combination with their low densities results in very favorable strength-to-weight ratios and their other desirable properties, do have a serious disadvantage in that they are susceptible to stress corrosion cracking at elevated temperature. Stress corrosion cracking can occur in commercial titanium base alloys when a surface of an article produced from such alloys is exposed to a chloride environment at elevated temperature and under stress. This may involve contact of the article surface with chlorine or chloride-containing gas or contact with salt or other chloride-containing materials or compounds. Specimens with a surface in contact with sodium chloride have shown stress corrosion cracking at a temperature as low as 525° F. under stress of 90% of yield strength for 2,000 hours. In an atmosphere of air containing 1% chlorine, stress corrosion has been induced at temperature as low as 200° F. upon exposure for only a few hours under stress. Even human fingerprints which contain a small amount of sodium chloride have caused stress corrosion cracking when fingerprinted articles of commercial titanium base alloys have been exposed, for example, to temperatures above about 525° F. under stress of 30,000 p.s.i. or more for an extended period of time.

Commercially pure titanium, unlike the commonly used titanium base alloys, is not susceptible to stress corrosion cracking. However, the strength of the more popular titanium base alloys and their other desirable properties, such as heat treatability, cannot be obtained or developed in commercially pure titanium. A serious need, therefore, exists for a titanium base alloy having mechanical properties comparable to or in the same range as those of now-produced alloys of its general type but which would be immune also to stress corrosion cracking in a chloride environment at elevated temperature.

Summarized briefly, this invention provides a titanium base alloy consisting essentially of from about 2.5% to about 7.5% zirconium, from about 2.5% to about 10% molybdenum, up to about 0.5% beryllium, with the balance substantially titanium. All percentages of alloy elements referred to herein are percentages by weight. The alloy as annealed is characterized by an ultimate tensile strength of at least 110,000 p.s.i. and tensile elongation of at least 3%. It is heat treatable and ageable to a strength at least 10% greater than in the annealed condition and is immune to stress corrosion cracking in a chloride environment at elevated temperature.

The alloy of this invention is of the alpha-beta type, its microstructure comprising a mixture of the alpha and beta phases at normal temperatures. Its annealed strength may be greatly enhanced by solution heat treating at temperature from about 200° F. below the beta transus of the alloy to about 100° F. above the beta transus followed by rapid cooling and then ageing between 900° F. and 1100° F. for from 15 minutes to 48 hours.

The particular alloying elements and the amounts in which they are present in the alloy of the invention are critical to obtain the particular combination of properties described above. Zirconium tends to stabilize the alpha phase in a two-phase titanium base alloy, but it also lowers the beta transus temperature. It needs to be present in amount of at least about 2.5% to provide strength increase without appreciable loss of ductility but should not be present in amount more than about 7.5% because above this level its effect on alloy density is a principal limitation.

Molybdenum is a beta stabilizer of the isomorphous type in that beta titanium and molybdenum are miscible in all proportions in the solid state. Its presence in the alloy of the invention substantially increases the tensile strength and imparts age-hardenability to the alloy. At least 2.5% molybdenum is necessary to obtain an appreciable strength increase; but above 10% molybdenum the additional strength increase obtained is accompanied by excessive loss in ductility.

Beryllium may be present in the alloy of the invention in amount up to about 0.5%. It is therefore an optional alloying element which is considered generally to be a beta stabilizer but with relatively low solubility

finished articles, such as bar, sheet, strip, wire or tubing and other shapes which may later be converted by additional working or forming procedures into final products or articles for commercial use.

After working or rolling, the alloy of the invention may be annealed to place it in best condition for further forming and fabrication and also for stress relief. Wrought products may be annealed at temperatures from about 1200° F. to about 1500° F. for a period of from about 15 minutes to 2 hours or longer followed by air cooling. It will be found, however, that an alloy according to the invention containing zirconium, molybdenum and beryllium, for example 2.5% Zr-7.5% Mo-0.25% Be, should preferably not be heated at a temperature of 1400° F. or higher since this, for reasons not known, appears to result in embrittlement. Alloys with and without beryllium can, however, be advantageously annealed at temperatures below 1400° F. and preferably from 1300° F. to below 1400° F.

Mechanical properties of alloys according to this invention are shown in Table 1, following, together with properties of a commercial titanium base alloy containing 6% aluminum and 4% vanadium, which is included for comparison.

TABLE 1

Alloy ¹	Ultimate tensile strength (p.s.i.)	Yield strength 0.2% offset (p.s.i.)	Elongation 1 inch, percent	Hardness VHN	Stress ² corrosion cracking
2.5% Zr, 7.5% Mo, Bal. Ti ³ -----	128,000	105,000	13	280	None.
2.5% Zr, 7.5% Mo, 0.25% Be, Bal. Ti ³ -----	134,000	131,000	11	306	Do.
5% Zr, 5% Mo, Bal. Ti ³ -----	117,000	100,000	8	260	Do.
7% Zr, 5% Mo, 0.25% Be, Bal. Ti ³ -----	131,000	124,000	7	297	Do.
Commercial, 6% Al, 4% V, Bal. Ti ³ -----	130,000	120,000	12	295	Cracked under test.

¹ Alloys melted and remelted to form an ingot which is forged then rolled to about 0.050" sheet and annealed at 1,450° F. for two hours followed by air cooling.

² Test samples exposed with surface in contact with sodium chloride at 1000° F. under stress for four hours and bend tested to determine cracking.

³ Annealed at 1,300° F. for one half hour followed by air cooling.

in titanium with resultant formation of intermetallic compounds at atmospheric temperatures. It is accordingly often classified as a "compound former." Its effect is to bolster the strengthening function of the zirconium and molybdenum, which will be found to reach a maximum at about 0.25% beryllium. At percentage levels above about 0.5%, beryllium will produce additional strengthening only with deleterious effect on the ductility of the alloy.

Incidental impurities may be present in the alloy of this invention. Such impurities will include the interstitials oxygen, nitrogen and carbon, as well as various metallic impurities present in the titanium and alloying metals in amounts which individually and in aggregate will not effect the essential characteristics of the alloy. Oxygen should not be present in amount more than about 0.3%, nitrogen not more than about 0.05%, and carbon not over about 0.05%. The interstitials in total amount should not exceed about 0.35%. Total incidental impurities, including interstitials and metallic elements, will not ordinarily exceed about 0.65%.

The alloy of the invention may be produced by conventional methods in which titanium metal is rendered molten in admixture with the desired proportions of recited alloying metals. Titanium metal in the form of sponge may be thoroughly mixed with zirconium, molybdenum, and optionally also beryllium, as subdivided metal particles, and the admixture compressed into compacts which are then welded into a consumable electrode. This electrode may be melted in a suitable type of cold mold arc furnace and the resulting ingot may be remelted to provide improved uniformity and homogeneity. The so-produced alloy ingot may be processed by conventional techniques such as forging, rolling and other working methods to produce intermediate mill products and semi-

Age hardening heat treatment of the alloy of the invention, or of an article produced from it, comprises first a solution heat treatment followed by rapid cooling and then an ageing step. The solution heat treatment is accomplished by heating the alloy or article to a temperature between about 200° F. below the beta transus of the alloy and 100° F. above the beta transus. Employment of a solution heat treating temperature between about 200° F. below the beta transus and the beta transus is preferred since this will generally produce better ductility than heating at a temperature above the beta transus. The alloy or article is maintained at solution heat treating temperature for a time sufficient to solutionize the alloy, that is, to insure complete solution of the alpha phase, but it is not held at this temperature so long as to result in excessive grain growth. Time at solution heat treatment temperature may advantageously be from one half minute up to about 60 minutes. Following solution heat treatment, the alloy or article is then rapidly cooled as by quenching, and this may be accomplished by quickly submerging the hot article in a water or oil bath. Following solution heat treatment and quenching, the alloy is then aged within the ranged of 900° F. to 1100° F. for from 15 minutes to 48 hours. Since ageing is a time-temperature effect, it is preferred to employ a temperature within the lower part of the ageing temperature range when employing a time within the upper part of the time range and to employ a temperature within the upper part of the temperature range when employing a time within the lower part of the time range. The solution heat treated and aged alloy article will have tensile strength at least 10% higher than that of the alloy in non heat-treated condition.

Typical properties for sheet materials similar to those of Table 1 but heat treated and aged are shown in Table 2, following. The alloys are immune to stress corrosion

cracking in the heat treated and aged condition, as they are as produced or annealed.

temperatures while exposed, for example, to salt spray or ocean atmospheres.

TABLE 2

Alloy	Heat treatment	Ultimate tensile strength (p.s.i.)	Yield strength 0.2% offset (p.s.i.)	Elongation 1 inch, percent	Hardness VHN
2.5% Zr, 7.5% Mo, Bal. Ti.	1,425° F.—10 min. WQ ¹ -----	143,000	121,000	5	304-312
	1,425° F.—10 min. WQ+1,000° F.—2 hr. AC. ²	161,000	156,000	2	319-317
	1,425° F.—2 hr. AC-----	173,000	155,000	2	345-357
	1,425° F.—2 hr. AC+1,000° F.—2 hr. AC.	150,000	146,000	3	319-314
	1,375° F.—10 min. WQ-----	174,000	158,000	3	360-342
2.5% Zr, 7.5% Mo, 0.25% Be, Bal. Ti.	1,375° F.—10 min. WQ+1,000° F.—2 hr. AC.	165,000	157,000	2	351-339
	1,375° F.—2 hr. AC-----	197,000	brittle	-----	401-413
	1,375° F.—2 hr. AC+1,000° F.—2 hr. AC.	168,000	162,000	1	345-357

¹ WQ=Water Quenched.
² AC=Air Cooled.

The reason for the stress corrosion cracking immunity of the alloy of this invention is not precisely known. We have discovered, however, that as a general rule titanium base alloys containing more than a limited small percentage of certain alloying elements cannot be employed without inducing stress corrosion cracking susceptibility. Zirconium and molybdenum appear to be unique in that they may be present in relatively large proportions and in combination up to 7.5% and 10% respectively without deleterious effect in this respect. Thus, these two elements in combination as described can be employed in sufficient amount to considerably enhance the strength of titanium without affecting their stress corrosion cracking immunity and while still retaining ductility in the alloy. The preferred composition, that is about 2.5% Zr-7.2% Mo-0.25% Be, balance titanium, will have strength, ductility and heat treatability of the same order as some widely used commercial titanium base alloys, such, for example, as the commercial alloy containing 6% Al-4% V, balance titanium; and with the additional unique and important advantage of stress corrosion cracking immunity.

The alloy of this invention and articles produced from it are useful in the production of parts and components for structures requiring light weight and high strength, such as airframes and jet engines, missiles and space vehicles. In addition, the alloy of this invention, because of its immunity to stress corrosion cracking in a chloride atmosphere, is particularly valuable when the end use of such alloys or articles involves exposure under stress to elevated temperature in a chloride environment. This may occur when aircraft or missiles are operated under conditions that their parts or surfaces reach relatively high

We claim:

1. An alloy consisting of by weight from about 2.5% to about 7.5% zirconium, from about 2.5% to about 10% molybdenum, up to about 0.5% beryllium, up to about 0.35% in total amount of the interstitials carbon, oxygen and nitrogen, balance titanium, characterized by an ultimate strength as annealed of at least 110,000 p.s.i. tensile elongation of at least 3%, and in being age hardenable to a strength at least 10% greater than in the annealed condition, and further characterized by high resistance to stress corrosion cracking in a chloride environment at elevated temperature.
2. An alloy according to claim 1 containing about 2.5% zirconium and 7.5% molybdenum.
3. An alloy according to claim 1 containing 0.25 to 0.5% beryllium.
4. An age hardened alloy according to claim 1 having an ultimate strength of at least 160,000 pounds per square inch, a tensile elongation of at least 2% and a microstructure consisting primarily of alpha titanium in a matrix of aged beta titanium.

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