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COLUMBIUM BASE ALLOYS

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This invention relates to columbium-base alloys containing small amounts of carbon.

Columbium-base alloys are known for their high-temperature strength and for their high-temperature oxidation resistance. The present invention is concerned with the discovery that if a small but critical amount of carbon is present in columbium-base alloys, it has the effect of significantly raising the embrittlement temperature of such alloys; i.e., for any given period of time, the alloys of this invention are able to withstand considerably higher temperatures without becoming embrittled. As a result of the use of carbon in the amounts herein specified in columbian-base alloys, it is possible to work and weld these alloys more readily and to utilize them at much higher temperatures than was previously possible.

The columbium-base alloys in which carbon can be used to raise the embrittlement temperature are those containing titanium and either molybdenum or tungsten, or mixtures of molybdenum and tungsten. The amount of carbon required is 0.02%–0.2% by weight of the alloy, with a range of 0.05%–0.15% being preferred.

Preferred alloy compositions possessing good high-temperature strength and oxidation resistance which are improved by the addition of 0.02%–0.2% of carbon are those containing 7–13% titanium, 7–18% molybdenum, the balance being essentially columbium. In these compositions, all or a portion of the molybdenum may be replaced on an atom-for-atom basis by the element tungsten.

Expressing these limitations in terms of weight percent compositions, the alloys of this invention comprise 0.02%–0.2% carbon, 7–13% titanium, and one of the group consisting of (1) 7–18% molybdenum, (2) 10–34% tungsten, and (3) 7–34% of a mixture of molybdenum and tungsten in which the molybdenum content is not greater than 18% of the total alloy composition, the balance being essentially columbium in an amount of at least 50%.

In a more specific embodiment, the alloys of this invention comprise 0.02%–0.2% carbon, 7–13% titanium, 7–18% molybdenum, the balance being essentially columbium.

In another embodiment, where tungsten replaces a portion of the molybdenum, the alloys comprise 0.02%–0.2% carbon, 7–13% titanium, 2–7% molybdenum, 15–30% tungsten, the sum of the molybdenum and tungsten being 7–34% of the total and the balance being essentially columbium.

In still another embodiment, where tungsten replaces all of the molybdenum, the alloy comprises 0.02–2% carbon, 7–13% titanium, 15–30% tungsten, the balance being essentially columbium.

The alloys which are herein described can be prepared by conventional procedures, such as by powdered metallurgy or by melting and casting techniques. For example, the individual metals can be melt-cast together and the melt allowed to cool and solidify into a desired shape. The required amount of carbon may be added in any convenient form, as for example lampblack, or graphite; or it may be added in combination with one of the metals used, as for example columbium carbide, titanium carbide, molybdenum carbide, or tungsten carbide. The

melting operation can be carried out in an arc melting furnace provided with consumable or nonconsumable electrodes, or by subjecting the charge to induction heating in a skull or specially designed crucible type of container. One useful form of arc melting furnace comprises that having an integral, water-cooled copper crucible in which the charge can be melted, and solidified, such as that described by W. Kroll in "Transactions of the Electrochemical Society," vol. 78, pages 35–47, 1940. Alternatively, a compressed, consumable arc electrode type melting furnace can be employed, such as described in U.S. 2,640,860 to S. A. Herres, as can the combination of a nonconsumable and consumable electrode type of double melting furnace described in U.S. 2,541,764 to S. A. Herres. A continuous-feed type of furnace can also be used, such as described in U.S.P.B. Report 111,083. Whatever the type of furnacing means employed, care should be exercised in the melting and casting operation to protect the molten metal from normal atmospheric contamination through contact with oxygen, nitrogen, etc. Contamination can be prevented by conducting the operation under a vacuum or an atmosphere of an inert gas, such as argon, helium, etc.

The individual metals charged to the melting furnace can be in any desired form, e.g. powder, grains, shot, wire, or sponge, and should be of commercially acceptable purity to insure production of a satisfactorily pure alloy product. Although preferably metals exhibiting relatively high purity are utilized herein, some variance in purity properties can be tolerated. Residual amounts of carbon are usually found in one or more of the metals used to prepare the alloy compositions. Therefore, it is pointed out that this residual carbon content of the alloy should be taken into consideration in adjusting the amount of carbon to 0.02%–0.2%. The alloys of the examples and those tested were prepared from commercially available columbium, titanium, and molybdenum. The carbon was added in some cases as commercially available columbium-carbide, and in some cases as commercially available graphite.

For a clearer understanding of the invention, the following specific examples are given. These examples are intended to be merely illustrative of the invention and not in limitation thereof. All percentages are in terms of weight and all tensile tests are according to the recommendations of the ASTM, Designation E8–54T.

EXAMPLE 1

An alloy of 10% Ti, 10% Mo, 0.025% C, balance Nb was prepared by melting together in an atmosphere of helium in a water-cooled, copper crucible of an arc-melting furnace 395.6 parts of columbium, 50.0 parts of titanium, 50.0 parts of molybdenum, 4.37 parts of columbium carbide. When the metals had become completely molten, the furnace was turned off and the melt was allowed to solidify and cool in the helium atmosphere. The alloy was then remelted and resolidified six additional times in order to insure thorough mixing of the ingredient metals. The casting was ultimately recovered in the form of the water-cooled copper crucible. The casting was machined to a round bar of approximately ½" diameter x 5".

In the same manner, other alloy samples were prepared in accordance with the compositions listed in Table I below. Each of the alloy samples prepared by melting and machining as described above was then swaged through a series of dies at the specified temperature, each die reducing the cross-section by 12½%. The results are given in Table I below.

Table I

INFLUENCE OF CARBON ADDITIONS ON WORKABILITY

Composition (percent)				Reduction in cross-sectional area without cracking (percent)		
Nb	Ti	Mo	C	Swaged at 1,000 ° C.	Swaged at 1,400° C.	Swaged at 600° C.
Bal.	10	10	0.025	50	50	50
Bal.	10	15	0.050	50	50	50
Bal.	7	10	0.10	50	50	50
Bal.	10	10	0.175	50	50	50
Bal.	10	10	0.20	50	50	50
Bal.	10	10	0.25	25	40	15
Bal.	10	10	0.50	(1)	(1)	(1)
Bal.	10	10	[2] 0.005	(1)	(1)	(1)

[1] Severe cracking. [2] Residual; not intentionally added.

EXAMPLE II

A series of alloy compositions was made up in the manner described in Example I and machined into bars approximately ½" in diameter x 5". These bars were heated in an electric furnace at 1100° C. and swaged to approximately 50% reduction in cross-sectional area. The alloys were then heated in a vacuum induction furnace for the times and at the temperatures given in Table II. After this heating, the alloy samples were tested at room temperatures for strength and ductility.

Table II

INFLUENCE OF HEAT TREATMENT ON PROPERTIES OF SWAGED C-CONTAINING ALLOYS

	Strength		Ductility	
	0.2% yield (p.s.i.)	Ultimate tensile (p.s.i.)	Percent elongation in ¾"	Percent reduction in cross section
Bal. Nb, 10% Ti, 10% Mo, 0.025% C:				
No heat treatment	93,000	97,000	5	11
1 hr. at 1,300° C	82,700	88,300	19	32
1 hr. at 1,400° C	87,000	98,400	20	22
15 min. at 1,500° C	87,700	95,400	9.3	10.3
30 min. at 1,500° C	91,900	98,400	7	7.4
Bal. Nb, 10% Ti, 10% Mo, 0.05% C:				
No heat treatment	95,000	102,000	20	55
1 hr. 1,300° C	82,000	93,000	28	58
1 hr. 1,450° C	86,700	95,700	10.7	11.6
15 min. 1,500° C	86,900	97,500	20	23.6
30 min. 1,500° C	86,700	97,200	17.3	30.7
Bal. Nb, 10% Ti, 10% Mo, 0.10% C:				
No heat treatment	100,000	113,500	29	35
1 hr. 1,300° C	80,400	92,800	27	21.5
1 hr. 1,400° C	81,400	92,500	23	15
1 hr. 1,450° C	83,000	102,000	24	46.6
1 hr. 1,500° C	86,700	97,900	11	11.5
1 hr. 1,500° C	86,700	97,200	18.7	18.7
1 hr. 1,600° C	88,800	99,000	18.6	20.8

The advantageous effect on these alloys of carbon addition within the range specified in this invention may be seen by comparison of these results with those given below for an alloy containing 0.005% C which was prepared and tested in the same manner as set forth above.

	Strength		Ductility	
	0.2% yield (p.s.i.)	Ultimate tensile (p.s.i.)	Percent elongation in 1"	Percent reduction in cross section
Bal. Nb, 10% Ti, 10% Mo, 0.005% C (residual):				
No heat treatment	97,000	104,000	25	48
1 hr. 1,400° C	81,500	82,000	2	2

EXAMPLE III

An alloy of 10% Ti, 10% Mo, 0.08% carbon, balance columbium was prepared by consumable arc-melting. A 3" billet of this composition was extruded at approxi-

material 1350° C. at an extrusion ratio of approximately 6 to 1. Part of this extrusion was machined to 1" diameter and swaged at 1000° C. to approximately 70% reduction in cross sectional area. Specimens of this swaged material were heat treated in vacuum at the various temperatures specified in Table III and tested at room temperature. The results of these tests are given in Table III.

An alloy of the same composition except that no carbon was added was similarly melted, extruded, and tested. Results of these tests are also included in Table III.

Table III

INFLUENCE OF HEAT TREATMENT AND C ADDITIONS ON PROPERTIES OF EXTRUDED ALLOYS

	Strength		Ductility	
	0.2% yield (p.s.i.)	Ultimate tensile (p.s.i.)	Percent elongation in ¾"	Percent reduction in cross section
10% Ti, 10% Mo, 0.08% C, bal. Nb:				
After swaging, no heat treatment	113,000	124,900	16	30
1 hr. at 1,400° C	85,800	96,000	35	63
1 hr. at 1,500° C	87,000	96,300	35	58
1 hr. at 1,600° C	89,800	99,400	32	53

NOTE.—10% Ti, 10% Mo, bal. Nb: 1 hr. at 1,400° C.—Embrittled. Failed in tensile testing before yield strength was reached.

EXAMPLE IV

Part of the extruded stock from Example II was forged to approximately 0.10" sheet. The surfaces of the forging were cleaned and the sample was heat treated in vacuum for 1 hour at 1400° C. The heat-treated sample was cold rolled to 0.040" strip and the rolled strip was heat treated a second time at 1400° C. for 1 hour. A room temperature bend test was then made. The sample was bent 180° without cracking.

A similar alloy sample but containing no added carbon was melted, extruded and forged in the same manner. The sample was heat treated for 1 hour in vacuum at 1400° C. An attempt was made to cold roll the heat-treated sample, but it cracked badly and could not be rolled to sheet. An additional sample of the same alloy without heat treatment was rolled to 0.040" sheet. This strip was then heat treated for 1 hour in vacuum at 1400° C. at room temperature and in a bend test the sample broke immediately on loading.

EXAMPLE V

An alloy bar of 10% Ti, 10% Mo, 0.10% C, balance columbium was prepared according to the procedure described for Example I. The alloy bar so prepared was heated in an electric furnace and rolled to 0.100" sheet. The strip was ground to 0.060" and heat treated for one hour at 1400° C. Two sections of this sheet were electron-beam welded in a vacuum of less than 10^{-4} mm. Hg with 15 kilovolts and 105–110 milliamps. at a welding speed of 49 inches per minute. Rectangular specimens were cut from the welded material so that the weld bead was transverse to the specimen axis. At several temperatures, the specimens were bent around a mandrel, with the mandrel directly beneath the weld bead, to determine the minimum temperature at which a 90° bend could be obtained without fracture. A transition from ductile (90° bend) to brittle (less than 40° bend) occurs at —75° C.

An alloy sample of similar composition but with no carbon added was tested in the same manner. The transition temperature was found to be +55° C.

EXAMPLE VI

An alloy sample of 10% Ti, 10% Mo, 0.05% C, balance columbium was prepared for welding as given in Example V. The sheet in this case was rolled to 0.040"

and was electron beam welded in a vacuum of less than 10^{-4} mm. of Hg with 15 kilovolts and 45 milliamps. at a welding speed of 22 inches per minute. Rectangular specimens were cut from the welded material so that the weld bead was transverse to the specimen axis. At several temperatures, the specimens were bent around a mandrel, with the mandrel directly beneath the weld bead, to determine the minimum temperature at which a 90° bend could be obtained without fracture. A transition temperature of —150° C. was found for the alloy of this example. The transition temperature of an alloy of the same composition but without the added carbon was found to be —20° C.

EXAMPLE VII

Part of the extruded stock from Example III was forged into a plate to approximately 0.100" thick. The surfaces of the plate were cleaned and the sample was heat treated in vacuum at 1400° C. The heat-treated sample was cold rolled to 0.04" strip. One piece of the rolled strip was heat treated in vacuum for one hour at 1400° C., and another piece was heated for one hour at 1500° C. Both specimens showed 23% elongation (in ¾" gauge length) in room temperature tensile tests.

EXAMPLE VIII

Alloys having the composition set forth in Table IV were prepared by arc-melting. 3" billets were then extruded at 1550° C. at an extrusion ratio of approximately 6:1. The extruded alloys were swaged at 1100° C. to 70% reduction in cross section area. Portions of these swaged materials were heat treated in vacuum for the times and at the temperatures given below and were tested at room temperature. The results of these tests are given in Table IV.

Table IV

INFLUENCE OF HEAT TREATMENT ON DUCTILITY OF Nb-Ti-Mo-W-C ALLOYS

	Strength		Ductility	
	0.2% yield (p.s.i.)	Ultimate tensile (p.s.i.)	Percent elongation in ¾"	Percent reduction in cross section
Bal. Nb, 10% Ti, 6% Mo, 20% W, 0.0065% C (residual):				
1 hr. at 1,300° C	135,800	145,300	[1] 9	[2]
1 hr. at 1,400° C	[3]			
Bal. Nb, 10% Ti, 6% Mo, 20% W, 0.005% C (residual):				
1 hr. at 1,300° C	143,900	153,800	[1] 10	[2]
1 hr. at 1,400° C	130,000	132,400	4	6
Bal. Nb, 10% Ti, 6% Mo, 20% W, 0.1275% C:				
1 hr. at 1,300° C	127,400	139,900	17	30
1 hr. at 1,400° C	118,400	127,300	12	15
1 hr. at 1,500° C	117,400	123,000	9	13

[1] Approximately.
[2] Specimen broke into several pieces.
[3] Broke before yield strength was reached.

It will be seen from the above examples that extremely valuable alloys have been produced by the addition of small amounts of carbon to columbium-base alloys comprising titanium, molybdenum, and tungsten. By the application of this invention to high-temperature oxidation-resistant alloys, it has been possible to increase the time and temperature of service of such alloys.

The alloys of this invention will be found particularly valuable in applications where a highly fabricable, ductile, strong, and oxidation-resistant material is required. Particularly, the alloys will be found useful where equipment is to be used at high temperatures, and in which it is especially desirable to retain such properties as strength and ductility at low temperatures after high-temperature service. The alloys herein described are exceptionally useful in applications requiring sheet and in which cupping, forming, and welding are necessary. The alloys of this invention have been found particularly suitable for use in high-temperature equipment, such as turbine vanes, flame holders, high-speed aircraft skin, after-burner liners, and chemical reactors and their accessories.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A columbium-base alloy consisting essentially of, by weight, 0.02%–0.2% carbon, 7–13% titanium, and one of the group consisting of (1) 7–18% molybdenum, (2) 10–34% tungsten, and (3) 7–34% of a mixture of molybdenum and tungsten in which the molybdenum content is not greater than 18% of the total alloy composition, the balance of this alloy composition being essentially columbium, the amount of said columbium being at least 50% of the total alloy.

2. A columbium-base alloy consisting essentially of, by weight, 0.02%–0.2% carbon, 7–13% titanium, 7–18% molybdenum, the balance being essentially columbium.

3. A columbium-base alloy consisting essentially of, by weight, 0.02%–0.2% carbon, 7–13% titanium, 2–7% molybdenum, 15–30% tungsten, the sum of the molybdenum and tungsten being 17–34% of the total, the balance being essentially columbium.

4. A columbium-base alloy consisting essentially of, by weight, 0.02%–0.2% carbon, 7–13% titanium, 15–30% tungsten, the balance being essentially columbium.

5. A columbium-base alloy consisting essentially of, by weight, 0.02%–0.2% carbon, about 10% titanium, about 10% molybdenum, the balance being essentially columbium.

6. A columbium-base alloy consisting essentially of, by weight, 0.02%–0.2% carbon, about 10% titanium, about 6% molybdenum, about 20% tungsten, the balance being essentially columbium.

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