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COLUMBIUM BASE ALLOYS

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The present invention relates to improved columbium-base alloys, and more particularly relates to such alloys consisting essentially of relatively large amounts of oxygen, relatively small quantities of either titanium or zirconium, balance columbium.

Our invention is based upon our surprising discovery that the addition of substantial amounts of oxygen as an intentional alloying element greatly improves the mechanical and physical properties of columbium when such columbium also contains small amounts of either titanium or zirconium.

As is well known to those skilled in this particular art, the metal columbium (which at times is also referred to as niobium) is characterized by a number of mechanical and physical properties which make it particularly suitable for use as a structural material at temperatures above 2000° F. Principal among such properties are its low density (8.57 g./cm.³ at 20° C.), a high melting point (2468±10° C.) and good fabricability. In addition it is further characterized by a low neutron capture cross section, a feature which is important in nuclear reactor construction. Furthermore, the metal fortunately is found in sufficiently good supply to be used where needed.

A number of columbium alloys have been made. Such alloying has been done in most cases in the attempt to improve the high temperature strength of the metal and in fact, alloys have been fabricated which do have considerably higher strength at elevated temperatures than does the unalloyed metal. However, such strengthening has been accomplished at the expense of added difficulties in alloy preparation and fabrication. Waste metal is expensive as a result of these alloying induced problems. Apparently the strengthening which is obtained by such alloying as taught by the prior art is obtained primarily with elements that enter into the columbium lattice structure as substitutional solutes, and because the refractory metals which are suitable for this use differ greatly from columbium and from one another in density and in melting point, there oftentimes results inhomogeneous melts and segregation during freezing.

In contradistinction to the teachings of the prior art, we have now discovered that the addition of very modest amounts of either titanium or zirconium and the ternary alloying of oxygen therewith markedly improves the properties of the columbium base metal.

Accordingly, a primary object of our invention is to provide a group of novel columbium alloys which are characterized by the strengthening of the base columbium metal by the dispersion strengthening effect of oxide phases therein.

Another more specific object of our invention is to provide a novel group of columbium-titanium-oxygen and columbium-zirconium-oxygen alloys.

These and other objects, features and advantages of our

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invention will become apparent to those skilled in this particular art from the following detailed disclosure thereof.

As noted above, the alloys of the present invention have a relatively insignificant quantity of substitutional solute contained therein. In the alloys of the prior art strengthening of the base metal is obtained with elements that enter the columbium lattice structure as substitutional solutes; in the present alloys, on the other hand, there are only the small quantities of substitutional solute and strengthening is obtained by the interstitial solute oxygen and by the dispersion strengthening effect of oxide phases. We recognize that small amounts of interstitially soluble elements are normal impurities in columbium and we recognize further that in the presence of elements more reactive than columbium such interstitially soluble elements form precipitate phases which contribute a strengthening effect. However, our invention entails the addition of considerably larger quantities of oxygen than that which is found in the normal impurity. Such large quantities of oxygen greatly enhance the strength of the columbium alloy and thus by the teachings of our invention the large addition of substitutional solutes can readily be avoided.

It is known that the high oxygen content in otherwise pure columbium has a marked embrittling effect. With this feature in hand, then, essentially the success of our invention is dependent upon the ability of the metals titanium or zirconium to combine with much of the oxygen that we add and to form a precipitate phase of suitable size, distribution, and stability which leads to relatively ductile columbium alloys while at the same time retaining the advantages of improved physical and mechanical properties. The compositions that are hereinafter specifically disclosed and other compositions made in accord with the teachings of our invention are characterized by such desirable aspects.

In carrying out the experimental work which led to this invention a high purity columbium sheet was used as melt stock. Oxygen was added thereto in the forms of high purity titanium dioxide and zirconium dioxide powders, and in addition titanium or zirconium sponge metal was added as required to achieve the desired final compositions. Four 225 gram melts were made of each alloy. Melting was performed in an arc furnace equipped with a water-cooled tungsten electrode and water-cooled copper crucible. During melting an inert atmosphere was maintained (argon or helium or mixtures thereof, for example, are quite satisfactory), and each ingot was inverted and remelted four times in order to assure homogeneity thereof.

The pancake shaped ingots resulting from such procedure were then heated in a protective atmosphere, removed and hammer forged to ½ in. bar on flat dies with reheating as necessary. It is readily apparent that this constitutes a rather severe forgeability test. Cb-1.5Ti-0.50 oxygen was forged at 1200° C.; Cb-1Zr-0.25O at 1050° and 1200° C.; Cb-3Zr-0.25O at 1200° and 1300° C.; and Cb-3Zr-0.50O at 1300° C.

Short-time tensile tests were performed in inert atmospheres on specimens machined from the as-forged bars, with the following results.

Nominal alloy composition (wt. percent)	Test temperature		UTS (p.s.i.)	-YS (p.s.i.)	Percent E1	Percent RA
	° F.	-° C.				
Cb-1.5Ti-0.50O	2,200	1,204	26,900	24,000	20	-----
Cb-1.5Ti-0.50O	2,000	1,093	34,400	32,000	23	-----
Cb-1.5Ti-0.50O	2,000	1,093	31,400	29,000	13	-----
Cb-1.5Ti-0.50O	2,000	1,093	29,900	27,000	19	-----
Cb-1.5Ti-0.50O	1,800	982	36,500	33,000	14	-----
Cb-1.5Ti-0.50O	1,600	871	44,600	40,000	19	65
Cb-1.5Ti-0.50O	RT	RT	73,500	60,000	29	74
Cb-1.5Ti-0.50O	-76	-60	89,200	64,000	16	30
Cb-1.5Ti-0.50O	-76	-60	94,400	64,000	29	59
Cb-1Zr-0.25O	2,000	1,093	32,500	30,000	26	-----
Cb-1Zr-0.25O	2,000	1,093	34,500	32,000	10	-----
Cb-1Zr-0.25O	1,800	982	45,300	42,000	17	-----
Cb-1Zr-0.25O	RT	RT	76,900	68,000	16	54
Cb-1Zr-0.25O	-76	-60	88,700	-----	17	15
Cb-3Zr-0.25O	1,600	871	55,700	53,000	6	40
Cb-3Zr-0.25O	1,400	760	56,000	49,000	7	41
Cb-3Zr-0.25O	RT	RT	64,800	52,000	19	48
Cb-3Zr-0.25O	-76	-60	85,500	73,000	19	36
Cb-3Zr-0.50O	2,000	1,093	39,000	35,000	6	-----
Cb-3Zr-0.50O	2,000	1,093	42,500	39,000	5	-----
Cb-3Zr-0.50O	1,800	982	48,000	47,000	2	-----

For comparison, the properties of commercially pure columbium, vacuum arc melted and annealed have been reported as follows:

Test temperature, ° F.	UTS (p.s.i.)	0.2 YS (p.s.i.)	Percent E1	Percent RA
RT	48,410	36,000	48	63.5
1,600	15,180	9,400	47	96
2,000	10,100	8,100	34	100
2,200	11,230	9,900	33	78.9
	9,250	7,500	21	78.2

Within the present compositional ranges there are certain critical features. The larger additions of titanium are known to be detrimental to the high temperature strength of columbium alloys, and on the other hand large amounts of zirconium generally decrease the ductility at high temperature. Furthermore, the amount and distribution of precipitate oxide phases are sensitive to the proportions and absolute concentrations of the component elements. In addition, the properties of the resulting alloy are in turn a function of the size, quantity, and distribution of the precipitate. These alloys are therefore distinctly different from others which might be cited that contain the same elements but in substantially different concentrations. It might also be mentioned that differences in oxygen concentration of 0.1% or even less may be very important because oxygen has a low atomic weight compared to columbium and because strong bonds are developed between columbium and oxygen.

In view of the foregoing disclosure, it will be readily apparent to those skilled in this particular art the various modifications and variations may be affected without departing from the spirit or scope of the novel concepts of our invention.

We claim as our invention:

1. An alloy consisting essentially of from 0.25 to 0.50% oxygen a metal selected from the group 1.5% titanium and from 1% to 3% zirconium, balance columbium, wherein the ratio by weight of oxygen to titanium or zirconium ranges from 3 to 1 to 12 to 1 and wherein alloy strengthening is obtained by interstitial solute oxygen and by the dispersion strengthening effect of oxide phase.

2. An alloy consisting essentially of from 0.25 to 0.50% oxygen, 1.5% titanium, balance columbium, wherein alloy strengthening is obtained by interstitial solute oxygen and by the dispersion strengthening effect of oxide phase.

3. An alloy consisting essentially of from 0.25 to 0.50% oxygen, from 1 to 3% zirconium, balance columbium, wherein alloy strengthening is obtained by interstitial solute oxygen and by the dispersion strengthening effect of oxide phase.

References Cited by the Examiner

UNITED STATES PATENTS

2,973,261 2/61 Frank ----- 75-174
3,027,255 3/62 Begley et al. ----- 75-174

OTHER REFERENCES

Metal Progress, June 1960, article by Jahnke et al. (pages 69-74 relied upon).

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