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COLUMBIUM BASE ALLOY

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This invention relates to a columbium base alloy containing tantalum and tungsten as the major alloying ingredients.

The development of rockets and missiles and advances in nuclear reactors and gas turbines necessitate the use of materials of construction under extreme conditions of temperature and operation. It is necessary under these conditions to have superior alloys which combine workability, high-temperature strength and high-temperature oxidation resistance in an alloy.

Accordingly, it is an object of the present invention to provide an alloy which is characterized by resistance to high-temperature oxidation even at temperatures in excess of 1100° C.

It is another object of the present invention to provide an alloy which is amenable to heat treatment by conventional means.

Still another object of the present invention is to provide an alloy which, when exposed to an oxidizing atmosphere at elevated temperatures forms a pellicular metal oxide which adheres firmly to the alloy and is not substantially volatilized therefrom.

Other objects will be apparent from the subsequent disclosure and appended claims.

The alloy which satisfies the objects of the present invention consists essentially of a minimum of 27 weight percent of columbium, 10 to 50 weight percent tungsten, 5 to 40 weight percent tantalum, about 0 to 20 weight percent titanium, about 0 to 20 weight percent chromium, about 0 to 7 weight percent vanadium, about 0 to 5 weight percent iron, about 0 to 5 weight percent nickel, about 0 to 7 weight percent aluminum, about 0 to 5 weight percent cobalt, about 0 to 2 weight percent beryllium, about 0 to 5 weight percent zirconium, about 0 to 5 weight percent hafnium, about 0 to 2 weight percent barium, about 0 to 2 weight percent thorium, about 0 to 2 weight percent yttrium, about 0 to 2 weight percent of at least one rare earth metal, the sum total of titanium, chromium, aluminum, iron, nickel, cobalt and vanadium not exceeding 50 weight percent and the sum total of zirconium, hafnium, barium, beryllium, yttrium, thorium, and the rare earth metals not exceeding 6 weight percent; and incidental impurities.

While the foregoing alloy satisfies all the objects set forth above it has been found that an alloy consisting essentially of a minimum of 39 weight percent columbium, 10 to 35 weight percent tungsten, 5 to 30 weight percent tantalum, 0 to 15 weight percent titanium, 0 to 10 weight percent chromium, 0 to 5 weight percent vanadium, 0 to 5 weight percent iron, 0 to 3 weight percent nickel, 0 to 5 weight percent aluminum, 0 to 3 weight percent cobalt, 0 to 1 weight percent beryllium, 0 to 3 weight percent zirconium, 0 to 3 weight percent hafnium, 0 to 1 weight percent barium, 0 to 1 weight percent thorium, 0 to 1 weight percent yttrium, 0 to 1 weight percent of at least one rare earth metal, the sum total of titanium, chromium, aluminum, iron, nickel, cobalt and vanadium not exceeding 29 weight percent and the sum total of zirconium, hafnium, barium, beryllium, yttrium, thorium, and the rare earth metals not exceeding 5 weight percent and incidental impurities is particularly outstanding for use under oxidizing conditions particularly high-temperature oxidizing conditions since the alloy strongly resists reaction with oxygen at temperatures in excess of 1100° C.

The maximum benefits of the present alloy are obtained when the alloy consists essentially of a minimum of 40 weight percent columbium, 10 to 25 weight percent tungsten, 10 to 25 weight percent tantalum, 5 to 15 weight percent titanium, 0 to 10 weight percent chromium, 0 to 5 weight percent vanadium, 0 to 4 weight percent iron, 0 to 2 weight percent nickel, 0 to 5 weight percent aluminum, 0 to 3 weight percent cobalt, 0 to 1 weight percent beryllium, 0 to 3 weight percent zirconium, 0 to 3 weight percent hafnium, 0 to 1 weight percent barium, 0 to 1 weight percent thorium, 0 to 1 weight percent yttrium, 0 to 1 weight percent of at least one rare earth metal, the sum total of titanium, chromium, aluminum, iron, nickel, cobalt and vanadium, not exceeding 25 weight percent and the sum total of zirconium, hafnium, barium, beryllium, yttrium, thorium, and the rare earth metals not exceeding 5 weight percent; and incidental impurities.

The alloys having the above compositions are particularly suitable for short-time, ultrahigh temperature applications where oxidation resistance, while being important, is less important than high strength at the elevated temperatures employed.

The alloys of the present invention may be prepared by any number of methods such as the conventional methods using inert operating conditions, e.g., by the consumable arc-melting technique described in U.S. Patent No. 2,640,860, by non-consumable arc welding, by pressing and sintering of metallic powders or by other powder metallurgical processes. Great caution should be exercised to protect the metals from the atmosphere since contamination of the alloying mass by nitrogen and oxygen, etc. destroys many of the valuable properties of the alloy. To protect the alloying materials from these atmospheric contaminants the alloying operation should be performed under vacuum or in an inert atmosphere, such as argon or helium, or under a protective slag or under a combination of protective slag and controlled atmosphere. The final shaping of the alloy metal may be accomplished after cooling by any of several procedures, such as, extrusion, swaging, rolling or grinding the cast or sintered shape.

The examples provided below were prepared in a non-consumable arc furnace such as that described by W. Kroll in Transactions of the Electro-Chemical Society, volume 78, 1940, pages 35 through 47. The procedure consists of placing the component metals on a water cooled, copper crucible shaped to retain the charge in a hearth like depression and incorporated in a gas tight container supplied with a tungsten electrode capable of impressing an arc onto the charge. After careful evacuation of the system the charge was melted four times under an argon atmosphere until a homogeneous alloy of the desired composition was obtained.

The oxidation resistance of the alloy was determined by exposing highly polished specimens measuring approximately 1.60 x 0.85 x 0.65 centimeters to a stream of pure, dry oxygen within an air tight container. The specimens were suspended and heated in this atmosphere at 800° C., 1000° C. or 1200° C. and the amount of pellicular metal oxide formed on the surfaces during the exposure was continuously measured and recorded automatically by means of balances of the Mauer type. By this method an accurate rate of oxidation weight gain could be obtained for the alloys tested. The weight gain is expressed in milligrams of weight gained per square centimeter of surface exposed for at least 100 hours at the different temperatures.

EXAMPLE I

A homogeneous melt containing 65 percent columbium, 10 percent tantalum, and 25 percent tungsten was prepared by melting the above-cited elemental metals together in the manner set forth above, and the alloy so

prepared was tested for its oxidation resistance. Under these conditions, the alloy showed a 100-hour weight gain of 445 mg. per square cm. at 1200° C. Unalloyed columbium shows a weight gain of 24,000 mg. per square cm. at 1200° C. under identical testing conditions.

EXAMPLE II

An alloy containing 70 percent columbium, 20 percent tantalum, and 10 percent tungsten was prepared and tested for oxidation resistance according to the procedure set forth in Example I. The 100-hour weight gain, expressed in mg. per square cm. was determined to be 475 at 1200° C.

EXAMPLE III

Adopting the procedures used in Example I, an alloy was prepared containing 65 percent columbium, 20 percent tantalum, and 15 percent tungsten. Upon testing for its oxidation resistance, the 100-hour weight gain, expressed in mg. per square cm., was found to be 512 at 1200° C.

EXAMPLE IV

Following the procedure described in the foregoing examples an alloy having the composition of 47 weight percent columbium, 20 weight percent tantalum, 20 weight percent tungsten, 10 weight percent titanium and 3 weight percent vanadium was prepared. This alloy showed a 100-hour weight gain at 1200° C. of 240 mg. per square centimeter.

EXAMPLE V

Following the procedure described in the foregoing examples an alloy having the composition of 45 weight percent columbium, 20 weight percent tantalum, 25 weight percent tungsten, 5 weight percent titanium, 3 weight percent aluminum and 2 weight percent vanadium was prepared. This alloy showed a 100-hour weight gain at 1200° C. of 193 mg. per square centimeter.

EXAMPLE VI

Following the procedure described in the foregoing examples an alloy having the composition of 45 weight percent columbium, 20 weight percent tantalum, 25 weight percent tungsten, 5 weight percent titanium, 3 weight percent iron and 2 weight percent nickel was prepared. This alloy showed a 100-hour weight gain at 1200° C. of 107 mg. per square centimeter.

EXAMPLE VII

Following the procedure described in the foregoing examples an alloy having the composition of 45 weight percent columbium, 20 weight percent tantalum, 25 weight percent tungsten, 5 weight percent aluminum and 5 weight percent vanadium was prepared. This alloy showed a 100-hour weight gain at 1200° C. of 154 mg. per square centimeter.

Although it is preferable to use high-purity metals in the preparation of the alloys of the present invention, a small amount of variance in purity can be tolerated before product quality suffers appreciably. The alloys of the working examples are prepared from commercially available metals which contain a small percentage of incidental impurities.

While all of the foregoing alloys have been found to be extremely oxidation resistant it has been found further that when up to 10 percent of molybdenum is added to the alloy the oxidation resistance is still further enhanced. Best results are obtained when about 1 to about 5 percent molybdenum is employed and particularly when the molybdenum content is about 3 percent.

Within the compositional ranges set forth above certain specific compositions have been found to have exceptional properties. These compositions are shown in Table I.

Table I

ALLOY COMPOSITION

Percent Cb	47	40	47	47
Percent Ta	20	20	20	20
Percent W	20	20	20	20
Percent Ti	10	10	7	10
Percent V	3	5	3	------
Percent Al	------	5	------	------
Percent Fe	------	------	3	------
Percent Mo	------	------	------	3

As an example of the molybdenum-containing material an alloy was prepared containing 47 percent columbium, 20 percent tungsten, 20 percent tantalum, 10 percent titanium and 3 percent molybdenum. This material was subjected to pure oxygen at 1200° C. for 100 hours. The weight gain was 180 mg. per square centimeter.

What is claimed is:

1. An alloy consisting essentially of about 20 weight percent tantalum, about 20 weight percent tungsten, about 10 weight percent titanium, about 3 weight percent vanadium, the balance being columbium and incidental impurities.

2. An alloy consisting essentially of about 20 weight percent tantalum, about 20 weight percent tungsten, about 10 weight percent titanium, about 5 weight percent vanadium, about 5 weight percent aluminum, the balance being columbium and incidental impurities.

3. An alloy consisting essentially of about 20 weight percent tantalum, about 20 weight percent tungsten, about 7 weight percent titanium, about 3 weight percent vanadium, about 3 weight percent iron, the balance being columbium and incidental impurities.

4. An alloy consisting essentially of about 20 weight percent tantalum, about 20 weight percent tungsten, about 10 weight percent titanium, about 3 weight percent molybdenum, the balance being columbium and incidental impurities.

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