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3,131,059 CHROMIUM-TITANIUM BASE ALLOYS RESISTANT TO HIGH TEMPERATURES

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This invention relates in general to alloys capable of resisting high temperatures and more particularly, to alloys of such character well suited for the brazing of columbium and columbium base alloys and having additional utility as high temperature protective coatings and as casting alloys.

It has become increasingly important, particularly in aircraft applications, to use materials which are capable of withstanding extremely high temperatures. One such material is columbium, which is a refractory metal possessing a melting point in the vicinity of 4400° F. From a design standpoint, it is an excellent material because of its high strength to weight ratio in the 2000 to 2500° F. range of service temperatures. It does not strain-harden rapidly, allowing cold working up to 99% without annealing, and it is therefore particularly suitable for the forming of parts of complex shape. Columbium is also characterized by moderate density (comparable to iron and nickel), and a high melting point, with good strength retention above the useful range of currently available alloys.

Useful though it is in high temperature areas, joinder of the metal and its alloys presents problems. Thus, although it may be welded, nitrogen contamination is an obstacle since it causes an increase in the tendency for crater cracking, serious loss of ductility and an increase in the transition temperature. Welding also presents the problem of loss of strength due to recrystallization. In the handling of high strength columbium alloys, recrystallization occurs between 2200° and 2800° F., depending upon the alloy makeup. Welding involves these high temperatures and where recrystallization as a result occurs, a loss of approximately 50% in tensile strength may be anticipated.

However, it has been found that by using the alloys of this invention, excellent joinder of the metals is effected and a high temperature resistant joint is produced which is compatible with the strength characteristics of the joined materials. Argon gas is utilized to prevent oxidation of the columbium and its alloys during the brazing, only moderate efforts being necessary for purification of the gas preparatory to brazing.

The alloys of this invention are additionally useful as coatings for columbium and for other materials characterized by low oxidation resistance at elevated temperatures, i.e., of approximately 2000° F.

Further utility for these alloys is found in casting applications and in other areas of metal forming where adequate oxidation resistance at elevated temperatures is difficult to achieve and maintain and where both structural and non-structural provisions are a requirement.

Accordingly, it is an object of this invention to provide alloys well suited for the brazing of columbium and columbium base alloys, which alloys are capable of providing excellent joint strength at elevated temperatures.

It is another object of this invention to provide alloys of the character described which do not require excessively high temperatures for brazing and which possess adequate ductility.

A further object is to provide alloys, as described, which do not cause excessive erosion of columbium and columbium base alloys when applied thereto in brazing applications.

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Yet a further object is to provide alloys suitable as protective coatings for preventing oxidation of materials having a high susceptibility thereto at elevated temperatures.

Another object is the provision of alloys adapted to casting applications which call for materials possessing adequate oxidation resistance at elevated temperatures.

These and other objects and advantages of this invention will become apparent from the following description of the alloys and their characteristics and the claims directed thereto.

In general the alloys of this invention include as matrix elements chromium and either or both titanium and palladium in the percentage-by-weight ranges indicated.

Each of these matrix elements is characterized by its compatibility with columbium and the alloys thereof. An alloying element selected from the group consisting of germanium, vanadium, and gold and proportioned as set forth, is added to the matrix elements. The resulting alloys have produced brazed joints possessing excellent joint strength at high temperatures. This brazing has been effected without the use of extremely high temperatures. Ability of the alloys to withstand high temperatures with a minimum of deterioration has contributed to their further utilization as coatings, protecting against oxidation of materials susceptible thereto. Formability at practicable temperatures and the aforementioned excellent high temperature characteristics further dictate use of the alloys in the area of metal forming, particularly in casting applications. It is to be understood that percentages used herein in the specification and claims to describe ingredient proportions are percentages by weight unless stated to be otherwise.

Chromium, as an elemental constituent common to each of the alloys has been found to be quite compatible with columbium, forming a diffusion layer which is much like that formed by titanium, but which shows more interaction at the interface with the brazing alloy. As used herein, the general range of chromium is from about 25 to about 65% by weight of the alloy. A preferred range has been found to be from about 35 to about 45%. Superior alloy compositions have been established incorporating the specific proportions of chromium tabulated below.

Titanium has also been found to be a highly satisfactory alloy matrix element, being highly compatible with columbium and promoting formation of a narrow diffusion layer at the interface with the columbium. Its general range is from about 10% to about 67% by weight of the alloy. A preferred range is from about 35 to about 45%. Superior alloy compositions have been formulated incorporating titanium in the specific proportions indicated.

Palladium, like chromium and titanium, serves as a matrix element. Like chromium, it has been found to be quite compatible with columbium and forms a narrow alloy layer. It enters into the alloys of this invention in the general range of from about 5 to about 25%. Its preferred range is from about 10 to about 20%. Superior alloy compositions include palladium in the quantities set forth below.

Germanium and vanadium are major alloy elements the general ranges for which are respectively from about 1 to about 20% and from about 5 to about 20%. The preferred proportion for each is about 10%. Germanium shows no obvious harmful effects upon the alloy, its effects if any in this respect, being masked by other alloy elements. Vanadium shows a distinct inter-granular penetration which is, however, minor. Some solutioning of columbium occurs above 2600° F.

Gold enters into the alloy as an element which promotes active inter action but which is used only as a minor element. It has been found to be quite compatible

with columbium, forming an alloy layer and causing some solutioning of columbium above 2500° F. when present in a quantity in excess of 10% by weight of the alloy composition. It is helpful in promoting ductility of certain of the alloys. The range of gold entering into the alloys of this invention is from about 1 to about 20%. A preferred alloy composition includes about 10% gold.

Although the process for alloy formulation is subject to variation, the alloys of this invention have for test purposes been formulated by mixing the elemental ingredients together in the desired proportions in powder form. The mixture is subsequently briquetted into a compact and arc melted in a cold hearth copper crucible. If ductile, the alloy is then rolled to form a foil, or in the alternative, broken into a powder to be used in such form.

As formulated herein, the alloys of this invention have taken the powder form. Application is effected by mixing the powder alloy with polyvinyl alcohol in a slurry, which is then painted on the joint to be brazed. The alloy is then heated to a temperature above its melting point, using argon gas for protection against oxidation. As has been earlier mentioned, moderate efforts should be made to purify the argon gas. Herein this has been accomplished satisfactorily by passing the argon through a glass-activated alumina dryer, a -100° F. Dry Ice-acetone cold trap, and a closed zirconia tube filled with titanium strips and operating at 1750° F. The protection offered by the argon gas is important. Should atmospheric contamination occur it will be reflected in reduced flow and wetting of the brazing alloy.

For purposes of the tests the results of which are reflected in the tabulations below, brazed lap shear test specimens were made up using for the members to be joined a columbium alloy incorporating by weight 10% titanium and 10% molybdenum. Time at temperature prior to testing was 1 minute. Using an A-frame type of lap-shear tension test setup, failure was made to occur within 1 minute by steadily increasing the mechanical stress upon the specimen by means of a floating screw. Stress was measured by means of a load link in conjunction with a strain recorder. Specimens were confined under a protective argon atmosphere during heating, testing, and cooling.

Each of the alloys of this invention is set out in the table below with an indication both as to the general range of its ingredients and as to the specific composition of the particular alloy or alloys tested. Also shown are the alloy melting temperatures and the results of shear tests conducted at elevated temperatures with regard to each brazed joint.

No.	Alloy—General Range or Specific Composition	Composition, Percent by Weight						Melting Temp., ° F.	Jt. Shear Strength, p.s.i. @ 2,000° F.
		Cr	Ti	Pd	Ge	V	Gold		
1	General	35-65	20-64				1-15		
	Specific	45	45				10	2,630	10,360
2	General	35-65	20-64			1-15			
	Specific	45	45			10		2,540	12,310
3	General	35-65	10-60	5-25					
	Specific	40	40	20				2,500	5,990
	Specific	45	45	10				2,440	7,310
4	General	25-40	20-65	5-20		5-20			
	Specific	35	35	20		10		2,500	4,410
5	General	25-40	20-65	5-20	5-20				
	Specific	35	35	20	10			2,390	5,900
6	General	25-40	15-67	5-25			3-20		
	Specific	35	35	20			10	2,350	9,050

During these tests, a remelt temperature rise phenomenon was observed in connection with that alloy designated number 2 in the above tabulation of test results. That is to say the melting temperature of this particular brazing alloy by itself is 2540° F. However, in tests after brazing of the columbium lap shear specimen, it was found that the alloy did not remelt at 3000° F. Although similar tests were not conducted with respect to the other of the enumerated specimens, it is believed that

a similar phenomenon would be found to exist for each of them.

Numerous high temperature oxidation studies of the above alloys have been conducted. Visual and microstructural studies indicate the usefulness of these alloys as protective coatings for materials having low resistance to oxidation at elevated temperatures. Application of the alloys may be accomplished by painting or spraying the alloy in powdered form on the surface of the metal to be protected and then heating the coated assembly until the powdered alloy melts to form a continuous surface coating. Alloys numbers 1, 2, 3, 5, and 6 tabulated above each showed percent weight changes of less than five percent after 100 hours in 2000° F. air, indicating their quality as protective coatings.

It is the above qualities of the alloys of this invention which adapt them for use in metal forming applications. Quite obviously superior corrosion resistance is offered at elevated temperatures and with melting points as indicated, forming is not a problem. The alloys can be made up in the manner indicated above or in other conventional fashion and then formed.

What I claim is:

1. An alloy characterized by its ability to withstand high temperatures consisting of by weight from about 35 to about 65% chromium, from about 20 to about 64% titanium, and from about 6 to about 15% gold.

2. An alloy characterized by its ability to withstand high temperatures consisting of by weight about 45% chromium, about 45% titanium, and about 10% gold.

3. An alloy characterized by its ability to withstand high temperatures consisting of by weight from about 35 to about 65% chromium, from about 20 to about 64% titanium, and from about 1 to about 15% germanium.

4. An alloy characterized by its ability to withstand high temperatures consisting of by weight about 45% chromium, about 45% titanium, and about 10% germanium.

5. An alloy characterized by its ability to withstand high temperatures consisting of by weight from about 35 to about 65% chromium, from about 20 to about 60% titanium, and from about 5 to about 25% palladium.

6. An alloy characterized by its ability to withstand high temperatures consisting of by weight from about 40 to about 45% chromium, from about 40 to about 45% titanium, and from about 10 to about 20% palladium.

7. An alloy characterized by its ability to withstand high temperatures consisting of by weight from about 25 to about 40% chromium, from about 20 to about 65% titanium, from about 5 to about 20% palladium, and from about 5 to about 20% vanadium.

8. An alloy characterized by its ability to withstand high temperatures consisting of by weight about 35% chromium, about 35% titanium, about 20% palladium, and about 10% vanadium.

9. An alloy characterized by its ability to withstand high temperatures consisting of by weight from about 25 to about 40% chromium, from about 20 to about 65% titanium, from about 5 to about 20% palladium, and from about 5 to about 20% germanium.

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10. An alloy characterized by its ability to withstand high temperatures consisting of by weight about 35% chromium, about 35% titanium, about 20% palladium, and about 10% germanium.

11. An alloy characterized by its ability to withstand high temperatures consisting of by weight from about 25 to about 40% chromium, from about 15 to about 67% titanium, from about 5 to about 25% palladium, and from about 3 to about 20% gold.

12. An alloy characterized by its ability to withstand high temperatures consisting of by weight about 35% chromium, about 35% titanium, about 20% palladium, and about 10% gold.

13. An alloy characterized by its ability to withstand high temperatures consisting of by weight from about 25 to about 65% chromium, from about 20 to about 67% titanium, and at least one ingredient in the range specified selected from the group consisting of germanium about 1 to about 20%, vanadium about 5 to about 20%, and gold about 6 to about 20%.

14. An alloy characterized by its ability to withstand high temperatures consisting of by weight from about 25 to about 65% chromium, from about 35 to about 45% titanium, and at least one ingredient in the range specified selected from the group consisting of germanium about 1 to about 20%, vanadium about 5 to about 20%, and gold about 6 to about 20%.

15. An alloy characterized by its ability to withstand high temperatures consisting of by weight from about 35

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to about 45% chromium, from about 35 to about 45% titanium, and at least one ingredient in the range specified selected from the group consisting of germanium about 1 to about 20%, vanadium about 5 to about 20%, and gold about 5 to about 20%.

16. An alloy characterized by its ability to withstand high temperatures consisting of by weight from about 25 to about 65% chromium, at least one ingredient in the range specified selected from the group consisting of titanium about 20 to about 65% and palladium about 20 to about 25%, and at least one ingredient in the range specified selected from the group consisting of germanium about 1 to about 20%, vanadium about 5 to about 20%, and gold from 5 to about 20%.

17. An alloy characterized by its ability to withstand high temperatures consisting of by weight from about 25 to about 65% chromium, from 10 to about 67% titanium, and from about 10 to about 20% palladium.

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