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ALLOYS RESISTANT TO HIGH TEMPERATURES

William T. Kaarlela, Fort Worth, Tex., assignor to General Dynamics Corporation, San Diego, Calif., a corporation of Delaware

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This invention relates in general to refractory metal alloys capable of resisting high temperatures and more particularly, to alloys of such character as may be well suited for the brazing of refractory metals such as columbium, tantalum, molybdenum, and their alloys, and having additional utility as high temperature protective coatings and as structural alloys.

It has become increasingly important, particularly in missile, spacecraft and aircraft applications, to use materials which are capable of withstanding extremely high temperatures. In addition to molybdenum and tantalum, 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 present problems. Thus, although it may be welded, nitrogen contamination is a deleterious 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. Vacuum environment or inert atmospheres such as argon gas are utilized to prevent oxidation of the columbium and its alloys during the brazing; only moderate efforts being necessary for purification of the argon 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 structural applications, such as castings, and in other areas of service 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 refractory metals such as columbium, molybdenum, tantalum, and their 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.

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

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 titanium as a matrix element in the percentage-by-weight ranges indicated. This matrix element is characterized by its compatibility with columbium, molybdenum, tantalum, and the alloys thereof. At least one alloying element selected from the group consisting of chromium, palladium, and at least one selected from the group consisting of silicon, and germanium and proportioned as set forth, is added to the matrix element. The resulting alloys have produced brazed joints possessing 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 and as barriers for protection against oxidation of various materials inherently susceptible thereto. Usable tensile strength of these alloys at temperatures around 2000° F. further dictate their use in the area of structural material, particularly in casting applications.

It is to be understood that percentages used herein in both specification and claims, to describe ingredient proportions, are percentages by weight unless otherwise stated.

Titanium as an elemental constituent to each of the alloys has been found to be quite compatible with the refractory metals forming a tough, narrow, diffusion layer at the interface with the brazing alloy. As employed herein, the general range of titanium is from about 20% to about 90% by weight of the alloy. A preferred range has been found to be from 30% to about 85%. Superior alloy compositions have been established incorporating the specific proportions of titanium tabulated below.

Chromium, like titanium, is quite compatible with the refractory metals forming a diffusion layer at the interface with the brazing alloy. As employed herein the general range for chromium is from about 20% to about 65% by weight of the alloy. A preferred range has been found to be 30% to about 48%. Superior alloy compositions include chromium in the quantities set forth hereinafter.

Palladium, like chromium and titanium, serves as a matrix element in certain of the present alloys. Like chromium, it has been found to be quite compatible with columbium and forms an interface alloy layer. It enters into the alloys of this invention in the general range of from about 5% to about 35%. Its preferred range is from about 10% to about 30%. Superior alloy compositions include palladium in the quantities set forth hereinafter.

Germanium serves to improve oxidation resistance and depresses the melting point, while silicon increases the high temperature shear strength and also serves as a melting point depressant. The general range for silicon is from about 5% to about 25%; the preferred range being about 6% to about 14%. For germanium, the general range is from about 5% to about 25%, and the preferred range is from about 7% to about 16%.

Although the process for alloy formulation is subject to considerable variation, the alloys of the present 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; then melted in a cold-hearth, water-

Further, each alloy was tested for structural integrity, brazing characteristics and environmental resistance. Such values as brazing temperature, re-melt temperature, shear strength, toughness factor and brazeability on columbium, molybdenum and tantalum were established and are set forth in tabular form below:

No.	Braze Temp. in ° F.	Joint Remelt Temp. ° F. on—		Shear Strength in Cb joint in p.s.i.		Toughness Index*	Brazeability on—		
		Cb	Ta	72°	2,000°		Cb	Mo	Ta
1-----	2,500	+3,300	+2,800	45,000	7,600	2,050	Good-----	Excellent--	Good.
2-----	2,700	+3,500	-----	25,000	23,800	1,920	Excellent--	Good-----	-----
3-----	2,700	+3,500	-----	24,000	23,100	-----	Excellent--	Good-----	-----

*Value of 2,000 or higher indicates good toughness.

cooled, copper crucible. If ductile, the alloy is then rolled to form a foil, or in the alternative, broken and crushed into a powder to be used in this 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 in a protective environment, such as in a vacuum or using an argon atmosphere or other suitable inert gases for protection against the detrimental effect of oxidation. As hereinabove stated, moderate efforts should be made to purify the argon gas, if best results are to be obtained. This has been accomplished satisfactorily, in the present instance, by passing the argon through 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 inert argon gas is important. Should atmospheric contamination occur it will be directly reflected in reduced flow and wetting of the brazing alloy, resulting in an inferior joint.

For purposes of the tests, the results of which are reflected in the tabulations below, brazed lap shear test specimens were made up using a columbium alloy incorporating by weight 10% titanium and 10% molybdenum. These were employed as the members to be joined and lap shear tested. Time at temperature prior to testing was 1-5 minutes. Employing an A-frame type lap shear tension test apparatus, failure was made to occur within one minute by steadily increasing the mechanical stress upon the specimen by means of a floating screw. Test temperatures were effected by the induction heating of a graphite susceptor surrounding the specimen. Stress was measured by means of a calibrated load link in conjunction with a strain recorder. Specimens were confined under protective, substantially inert, argon atmosphere during heating, testing and cooling.

Each of the alloys of this invention is set forth 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:

No.	General Range or Specific Composition	Ti	Cr	Pd	Ge	Cb	Si
1-----	General-----	50-88	-----	5-35	-----	-----	5-15
	Specific-----	70	-----	20	-----	-----	10
2-----	General-----	20-60	20-60	5-35	-----	-----	5-25
	Specific-----	35	35	20	-----	-----	10
3-----	General-----	25-65	25-65	-----	-----	-----	5-25
	Specific-----	45	45	-----	-----	-----	10

During these tests, a remelt temperature rise phenomenon was observed in connection with alloys designated Numbers 1, 2, 3, in the above tabulation of test results. That is to say the brazing temperature of these particular alloys ranges between 2500° F. and 2700° F. However, in tests after brazing of the columbium or tantalum T specimens, it was found that these alloys did not remelt between 2800 and more than 3500° F., the highest temperature checked. 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.

- I claim:
1. An alloy characterized by its ability to withstand high temperatures and consisting of from about 20% to about 60% titanium, from about 20% to about 60% chromium, from about 5% to about 35% palladium, and from about 5% to about 25% silicon.
 2. An alloy characterized by its ability to withstand high temperatures and consisting of from about 30% to about 48% titanium, from about 30% to about 48% chromium, from about 10% to about 30% palladium, and from about 7% to about 12% silicon.
 3. An alloy characterized by its ability to withstand high temperatures and consisting of about 35% titanium, about 35% chromium, about 20% palladium, and about 10% silicon.

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DAVID L. RECK, Primary Examiner.

WINSTON A. DOUGLAS, Examiner.