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3,128,178

TANTALUM-TITANIUM BASE ALLOY

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This invention relates to tantalum-titanium base metal alloys, particularly to such alloys which contain alloying metals of vanadium and nickel as essential components, which make the resulting alloys ductile and resistant to corrosion by hot oxidizing and hot non-oxidizing acids.

Alloys with the above properties are most useful for lining chemical reaction vessels, auxiliary equipment and connecting lines, which are exposed to hot phosphoric acid and hot sulfuric acid. Liquid phosphoric acid is recognized as an efficient catalyst for certain organic chemical reactions, including alkylation and isomerization and the polymerization of normally gaseous olefins. Corrosive attack appears to be the greatest with aqueous solutions of about 85% phosphoric acid. While considerable progress has been made in controlling corrosion in the presence of liquid phosphoric acid (see, for example, Kemp and Zeh Patent 2,653,177 and Piehl Patent 2,854,497), there is need for further improvement and particularly for alloys which are also resistant to corrosion in the presence of hot oxidizing acids such as sulfuric acid. Sulfonations, cleavage and hydrolysis reactions often employ hot sulfuric acid. The most corrosive concentration for hot aqueous solutions of sulfuric acid appears to be about 55% sulfuric acid.

Prior art alloys are poor in corrosion resistance in the presence of either or both hot phosphoric acid and hot sulfuric acid. Usually resistance to sulfuric acid corrosion is readily attained, but the characteristic of resistance to corrosion by hot phosphoric acid is difficult to add. Even more difficult is to retain these corrosion resistant characteristics in an alloy that is ductile and can be worked sufficiently so that it can be used without sole reliance upon casting as the method of shaping.

The metal alloy of this invention has the above desirable characteristics. It is a tantalum base alloy comprised by weight of about 10 to 30% titanium, 3 to 10% vanadium and 0.25 to 3% nickel. Preferably, for good workability and ductility, the alloy contains 20 to 25% titanium and 5 to 7.5% vanadium. Without vanadium, a tantalum-titanium-nickel alloy was extremely difficult to work, either in cold rolling or hot rolling with protective cladding. For use with the most corrosive hot phosphoric acid concentrations, i.e., about 85%, the alloy should contain at least 0.5%, and preferably about 1%, of nickel. Optionally, columbium and tungsten can be added. Up to 15%, and sometimes up to 25%, of columbium can be used where lighter weight is an important factor. Tungsten in amounts to 10% serves to increase further the resistance to hydrogen embrittlement as well as to stabilize and to add strength to the alloy. However, the alloy should contain no less than 30%, and preferably at least 50% of tantalum.

We have found that, as compared to high temperature air oxidation, corrosion in aqueous conditions such as with the above aqueous acids is much more sensitive to impurities in the metal components of the alloy. Hence, impurities in the alloy should be kept to a minimum for the best results. Most desirably, the carbon content of the alloy should be no more than 0.03%; the oxygen content, no more than about 0.05%; the nitrogen content, no more than 0.008%; the hydrogen content, no more than about 0.001%. In addition, no more than about 0.3% of the combined elements aluminum, chromium,

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iron, zinc, zirconium, cerium and other rare earth metals should be present.

The impurities are avoided by using pure components and inert atmospheres in the alloy preparations. Conventional melting and remelting techniques with inert controlled atmospheres of argon, helium and the like are employed. Arc furnaces with water-cooled copper hearths and non-consumable electrodes (e.g. 2% thoriated-tungsten tip) were used in the preparations described below. Measured amounts of the metal components were melted in such furnaces. The alloy compositions, all in terms of weight percent, were melted, the "button" of alloy inverted, and remelted four times before final cooling and solidifying. Alternatively, other furnaces and known melting techniques such as with continuous feed of metal components, inductive heating, or other means could be used with adequate protection against contamination.

In the following illustrative examples, most of the alloys were clad in 310 stainless steel to avoid oxidation at the high temperatures used in fabrication. Cladding was done by lathe machining the alloy "button" into circular discs, enclosing them inside a 3 x 3 x 1/4-inch steel sheet having a circular hole in the middle, and welding 2 3/4 x 2 3/4 x 1/8-inch steel plates on each side. The resulting metal "sandwiches" of alloys were rolled at 2000° F. The rolling was done in a Stanat two-high mill and the metal was reduced 7.5% to 15% per pass to a total of about 70%.

The alloys were tested for corrosion by exposing them to solutions of 55% sulfuric acid and 85% phosphoric acid sealed in heavy-wall Pyrex ampules. Alloy specimens were prepared by grinding, sanding and finishing of surfaces and edges, and degreasing. Surface areas (generally about 6.5 cm.²), weights and densities were then determined. The density was measured by weight-in weight-out of water method. The volumes of sulfuric acid and phosphoric acid solutions were 40 and 30 ml., respectively. Contaminations due to silica formation in the phosphoric acid tests were avoided by liners of Teflon tubing inside the glass ampules. The corrosion tests were for 72 hours. From the measurements of weight loss, density and surface area, the penetration or corrosion rates in mils per year (i.e., "m.p.y.") were determined.

The following table shows the results of tests carried out as described above:

Number	Composition, percent by weight				Corrosion rates, m.p.y.	
	Ta	Ti	V	Ni	55% H ₂ SO ₄ at 450° F.	85% H ₃ PO ₄ at 400° F.
1.....	70	25	5	0	2.5.....	67.
2.....	67.5	25	7.5	0	2.5.....	61.
3.....	69	25	5	1	Wt. gain. ¹	Wt. gain. ²
4.....	66.5	25	7.5	1	do. ¹	do. ²
5.....	68	25	5	2	do. ¹	do. ²

¹ Weight gain of about .001 gms./cm.².
² Weight gain of about .003 gms./cm.².

The above tests illustrate the need for nickel in the composition. In alloys Nos. 1 and 2 without nickel, the high penetration or corrosion rates in phosphoric acid show considerable hydrogen embrittlement. On the other hand, alloy compositions 3, 4 and 5 were ductile and were readily hot rolled to give slight weight gains in the corrosion tests. The weight gain shows the formation of an insoluble protective film on the metal surface. The weight gain becomes constant. For example, alloy No. 5, upon exposure to 85% phosphoric acid at 400° F. gained no further weight after continuing the run for 164 hours. Testing alloy No. 5 under the same conditions for a total

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of 336 hours showed that the constant weight was attained in 48 hours. Similarly, alloy No. 4 when tests in 55% sulfuric acid at 450° F. for a total of 168 hours reached a constant weight in about 48 hours. Unalloyed tantalum or the tantalum alloys Nos. 1 and 2 above show under such conditions a steadily increasing weight loss. The alloys of the present invention are therefore superior since corrosion and hence hydrogen embrittlement are minimized.

For comparison, an alloy without titanium and composed of 74% tantalum, 25% vanadium and 1% nickel recrystallized and cracked on attempted rolling at 2000° F. after cladding. Further, solutionizing of this alloy for 68 hours at 1900° F. did not improve the workability.

Other ductile tantalum-titanium base alloys which illustrate the corrosion resistance (to hot sulfuric and phosphoric acids) alloy compositions of the present invention are tabulated as follows:

[Composition, percent by weight]

Number	Ba	Ti	V	Ni	Cb	W
6.-----	74.5	15	10	0.5	-----	-----
7.-----	64	15	5	1	15	-----
8.-----	70	20	5	2	-----	3
9.-----	74	20	3	3	-----	-----
10.-----	45	25	7	2	20	1

These various ductile, corrosion resistant alloys of the present invention are preferably used as lining materials

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for vessels and other equipment. They can be applied after rolling or other suitable fabricating manner by conventional methods of welding, brazing, vacuum joining, and the like.

I claim:

1. A ductile metal composition resistant to the action of hot oxidizing and non-oxidizing acids and consisting essentially of, in percent by weight, 10-30% of titanium, 3-10% of vanadium, .25 to 3% of nickel, up to 25% columbium, up to 10% tungsten, and the balance essentially tantalum, with the tantalum being present in an amount of at least 30%.

2. A ductile metal composition resistant to the action of hot oxidizing and non-oxidizing acids and consisting essentially of, in percent by weight, 20-25% of titanium, 5-7.5% of vanadium, 0.5 to 3% of nickel, up to 25% columbium, up to 10% tungsten, and the balance essentially tantalum, with the tantalum being present in an amount of at least 50%.

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