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2,819,960

FORMABLE ACID RESISTANT TITANIUM ALLOYS

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This invention relates to titanium alloys, and more particularly to alloys containing titanium as the major constituent, which have good working properties and are highly resistant to corrosion.

While titanium metal is resistant to corrosion by most chemicals, it is rapidly attacked by fluoride salts and strong acids of the reducing type, including hydrochloric, hydrofluoric, sulfuric, phosphoric, oxalic, formic and trichloro acetic acids. For example, in boiling 20% hydrofluoric acid, the titanium corrodes at a rate well in excess of 1000 mils per year. At moderate temperatures, titanium resists corrosion by these acids only when they are very dilute, or when inhibitors of the oxidizing type are present in the acid or on the surface of the metal. The titanium alloys are generally more resistant than the unalloyed metal; however, in all but a few isolated instances the corrosion rate is prohibitive. There are many applications, particularly in connection with hot hydrochloric and hot sulfuric acid, in which titanium alloys and also other commercially available materials do not have satisfactory corrosion resistance. There has been a long felt need for a reasonably priced corrosion resistant metal which has good working properties for service in connection with the aforementioned concentrated acids.

The only known titanium alloys which are resistant to these strong acid solutions are described in U. S. Patent No. 2,614,041 of Walter L. Finlay. They are binary alloys, containing between 30 and 40% molybdenum, and corrode at a rate up to about 10 mils per year in boiling 20% HCl or 40% H₂SO₄. However, these Ti-(30-40%)Mo alloys tend to be quite brittle, especially toward the upper end of the specified molybdenum range, and as a result, are difficult to fabricate.

In accordance with the present invention, it has been found that titanium alloys containing vanadium or columbium or both in addition to molybdenum, are at least as resistant, and in most instances more resistant, to corrosion by the above-mentioned acids than the alloys disclosed in U. S. Patent No. 2,614,041. Furthermore, the hardness of the novel alloys is such that they are more easily worked than the alloys of the patent. More particularly, the present invention contemplates formable, corrosion-resistant alloys containing about 20 to 30% molybdenum, and about 1 to 25% vanadium or about 1 to 30% columbium, or up to 30% in total amount of vanadium and columbium, and the balance titanium.

In the present alloys, substantial amounts of titanium and molybdenum of the alloys of the Finlay patent are replaced by vanadium and/or columbium. It was found that large additions of vanadium or columbium to titanium metal alone did not appreciably improve the resistance of titanium to corrosion by boiling sulfuric or hydrochloric acids. The presence of molybdenum in substantial amounts is definitely necessary to impart corrosion resistance, although the molybdenum content of the present alloys is less than that of the binary alloys

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disclosed in the aforementioned patent. As an illustration, appreciable reductions in molybdenum content are possible when the vanadium or columbium additions are more than equivalent to the molybdenum replaced from a Ti-30% Mo alloy, for example.

While columbium and vanadium are thus partial substitutes for molybdenum, it has been found that the desirable very low rate of corrosion is dependent upon the presence of at least 20% molybdenum in the novel ternary or quaternary alloys. In the case of titanium-molybdenum-vanadium alloys, the molybdenum content is preferably between about 24 and 30%, since those containing less than about 24% molybdenum are slightly more difficult to work. Generally speaking, titanium-molybdenum-vanadium alloys in which molybdenum is below the preferred range, while entirely satisfactory from the standpoint of corrosion resistance, are the least easily formed of any of the alloys of the present invention. No such preferred range is apparent in the titanium-molybdenum-columbium alloys, and the ease with which they are formed is substantially the same over the 20 to 30% molybdenum range. The same is true of the present quaternary alloys.

In the ternary vanadium alloys, the content of this element is between about 1 and 25% by weight, with 5 to 20% being preferred. The ternaries containing columbium have a somewhat higher tolerance for that element than the corresponding vanadium-containing alloys, and columbium may be present from 1 to 30%. Vanadium and columbium presumably function in substantially the same manner to impart improved workability and corrosion resistance, and when both are present together, they may account for up to about 30% by weight of the quaternary alloy.

Several of the alloys of the present invention were given severe corrosion tests, along with samples of both Ti-30% Mo and Ti-40% Mo, and a Ti-25% Mo alloy. Several samples of each alloy were exposed for periods of 48 hours to boiling 40% sulfuric acid and to boiling 20% hydrochloric acid. The results are conveniently stated in terms of mils per year of corrosion as determined by weight loss of the specimens. Corrosion rate as well as Rockwell "A" hardness and rollability of each of the alloys is reported in the following table, with the results for Ti-30% Mo and Ti-40% Mo being the average of several tests.

Composition Percent, Balance Titanium	Hardness, Rockwell A	Rollability	Corrosion Rate in mils/year after 48 hours in boiling	
			40% H ₂ SO ₄	20% HCl
25Mo	61	good	3.4	3.9
30Mo	61-63	good to fair	2.6	9.1
40Mo	62-64	fair to poor	2.9	2.5
29Mo-5Cb	61.3	good	2.8	4.1
27Mo-10Cb	61.5	do	3.3	3.5
25Mo-15Cb	62.4	do	2.0	1.6
24Mo-20Cb	61.7	do	1.2	5.3
20Mo-30Cb	61.7	do	1.0	4.3
23Mo-5V	62	do	3.4	2.3
27Mo-10V	62	do	2.5	3.3
25Mo-15V	57	do	2.3	3.6
24Mo-20V	59	do	3.9	3.1
22.5Mo-25V	65	fair	4.8	6.7
21Mo-30V	64	do	8.5	12.9

1 Range of several samples.
2 Average of several samples.

The pattern in the titanium-molybdenum binary alloys is readily apparent. With increased molybdenum, corrosion resistance is improved but at the expense of workability of the alloy. The ternary alloys of the present invention, on the other hand, exhibit not only good workability, but also very high resistance to corrosion over

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the aforementioned molybdenum, columbium and vanadium ranges. The optimum columbium ternary of those reported from both standpoints, contains about 20% columbium and from 20 to 25% molybdenum and the balance titanium. The corresponding optimum vanadium alloy is more sharply defined at about 25% molybdenum and about 15% vanadium.

It will be seen from the above table that alloys were chosen having molybdenum contents near the upper end of the specified range, with columbium and vanadium near the lower ends of their respective ranges, and vice versa, which permitted a fairly narrow range of titanium content. However, this inverse relationship between molybdenum content and that of columbium and vanadium, while it may be preferred, is not necessary since the latter two elements are also substitutes for titanium.

Numerous alloys outside the above-specified ranges were tested, including those containing 0-30% molybdenum and up to 50% of columbium and vanadium each alone and in combination. However, those having a molybdenum content below about 20% with columbium and vanadium above about 30% were found to be substantially harder than those of the present invention, and were sufficiently difficult to work by presently known methods to preclude any commercial possibilities.

Since tantalum is a natural impurity in columbium, the possibility that this metal itself might produce the aforementioned desirable improvements in titanium-molybdenum alloys was considered. However, a titanium-40% tantalum alloy was found to corrode at a rate substantially of the order of unalloyed titanium. The corrosion rates, hardness, and rollability of Ti-30% Mo-2% Ta, Ti-25% Mo-5% Ta, and Ti-20% Mo-10% Ta were found to be approximately the same as those of corresponding Ti-Mo alloys without tantalum additions. It is thus apparent that tantalum by itself does not benefit or harm titanium-molybdenum alloys, but acts as an inert element.

Likewise, it was found that tantalum is similarly inert in the alloys of the present invention. Thus, a few percent of tantalum may permissibly be present therein along with columbium, and the appended claims are to be so interpreted.

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The novel, formable, corrosion-resistant alloys of the present invention are well suited for use in connection with corrosive salts and strong acids of the reducing type, and particularly as materials of construction for containing these corrosive chemicals. The alloys are easily formed into any desired shape as by rolling or stamping or by other conventional working methods.

"Titanium" as employed in the foregoing description and in the appended claims is intended to include not only highly pure titanium as prepared by the well-known "iodide" method, but also commercial titanium, which may contain one or more of the elements oxygen, nitrogen and carbon in amounts up to about 0.2% nitrogen, up to about 0.3% oxygen and up to 0.5% carbon.

What is claimed is:

1. A formable titanium alloy, characterized by a high resistance to corrosion by acids of the reducing type, containing about 20 to 30% molybdenum, at least one element selected from the group consisting of about 1 to 25% vanadium and about 1 to 30% columbium, the total amount of vanadium and columbium not exceeding 30%, and the balance substantially titanium.

2. A formable corrosion-resistant alloy containing about 20 to 30% molybdenum, about 1 to 25% vanadium, and the balance substantially titanium.

3. An alloy according to claim 2 containing at least about 24% molybdenum.

4. A formable corrosion-resistant alloy containing about 24 to 30% molybdenum, about 5 to 20% vanadium, and the balance substantially titanium.

5. A formable corrosion-resistant alloy containing about 20 to 30% molybdenum, about 1 to 30% columbium, and the balance substantially titanium.

6. A formable, corrosion-resistant alloy containing about 20 to 30% molybdenum, 1 to 30% in total amount of columbium and vanadium, the vanadium content not exceeding about 25% and the balance substantially titanium.

References Cited in the file of this patent

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