Nov. 13, 1962 M. STERN 3,063,835

CORROSION-RESISTANT ALLOYS

Filed June 18, 1959 2 Sheets-Sheet 1

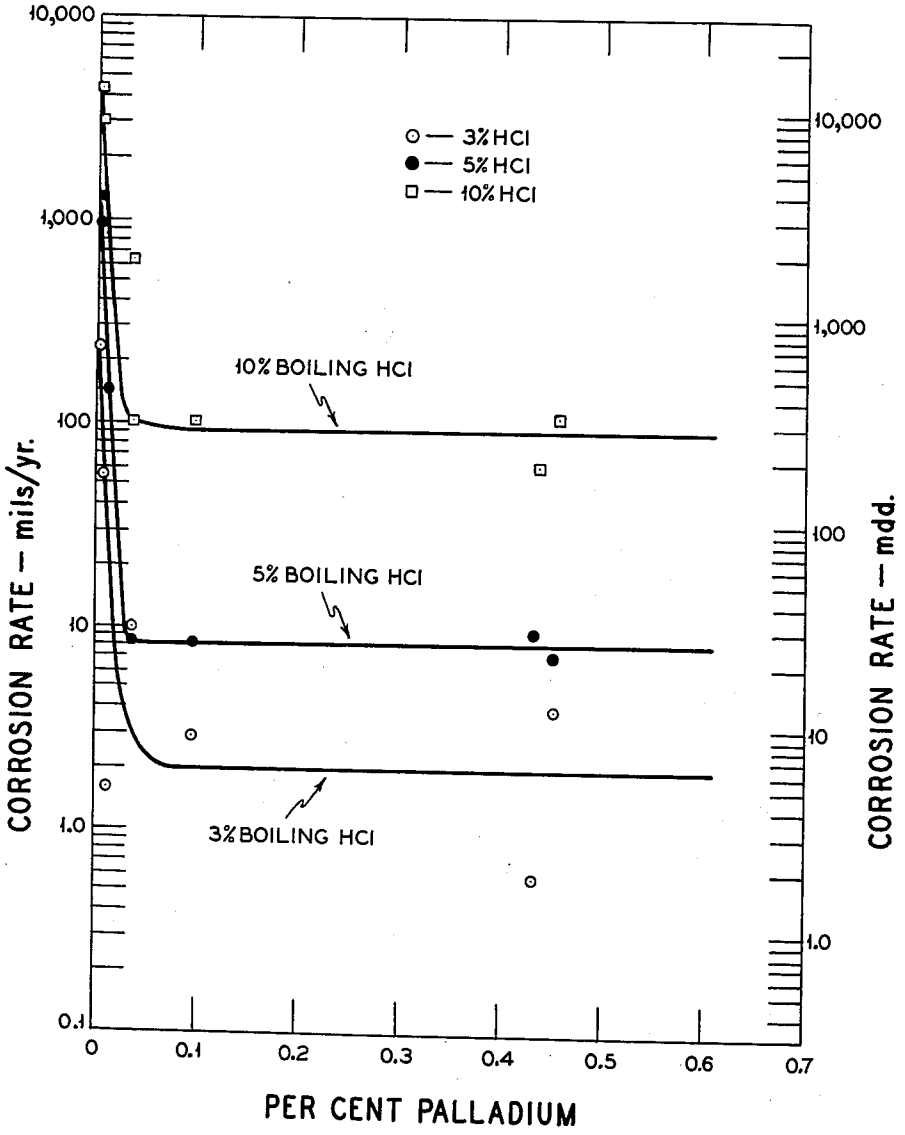

Fig. 1.

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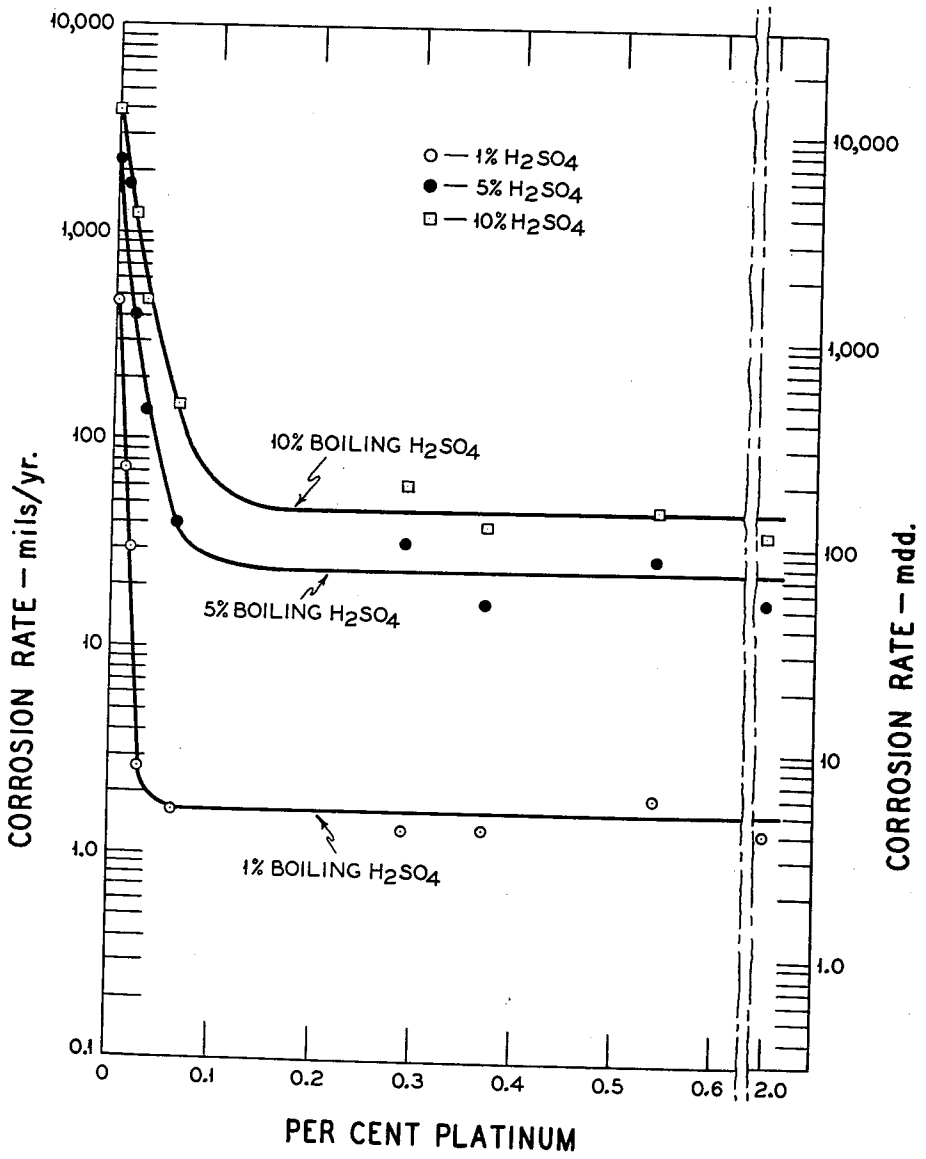

Fig. 2.

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CORROSION-RESISTANT ALLOYS

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10 Claims. (Cl. 75—175.5)

This invention relates to corrosion-resistant alloys and, particularly, to corrosion resistant alloys in which titanium or chromium is the predominant metal.

Titanium and many of its alloys, as well as chromium and many of its alloys are noted for excellent resistance to oxidizing corrosive media. In non-oxidizing corrosive media, such as hydrochloric and sulfuric acid solutions, these metals and alloys exhibit little or no resistance. It would be most desirable to have available alloys capable of withstanding corrosive environments ranging from strongly oxidizing to weakly oxidizing or non-oxidizing. An alloy of this type would have the widest utility. For example, such an alloy would be invaluable in chemical plant equipment.

Hydrochloric and sulfuric acids are prime examples of non-oxidizing corrosive media. These acids enter into many important commercial processes. They require storing and handling equipment which combine the desirable properties cited above. If a titanium alloy, for example, were to possess resistance to non-oxidizing acid solutions, in addition to its natural endowments of lightness, strength, and resistance to oxidizing acid solutions, it would be extremely useful in such applications.

There have been attempts to design titanium alloys specifically to resist attack by a strong non-oxidizing acid. Most typical among these are compositions of 30 to 40 percent molybdenum, balance substantially all titanium. The corrosion resistance is derived in great measure from the molybdenum which is itself resistant to these acids, but the effectiveness of the molybdenum does not become especially significant until amounts up to 20 percent are added. One disadvantage of this alloy is that the tendency toward brittleness increases along with molybdenum content so that by the time 40 percent is reached, the alloy has become excessively brittle and difficult to fabricate. Moreover, as resistance to non-oxidizing acids is gained, the resistance to oxidizing acids is lost.

One widely used method for preventing corrosion is to add passivating inhibitors to the environment which, it is believed, operate by producing local action current to anodically polarize a metal into the passive potential region. It is not always desirable, however, to alter the composition of a solution to prevent corrosion of the equipment in which it is contained, particularly when the composition of the solution is critical or specific to some process. Such a means of preventing corrosion is limited to the particular case where the composition of the contained solution is not critical.

According to scientific theory, corosion resistance can be achieved in non-oxidizing environments by artificially anodically polarizing the base metal by applying an external current (which might be termed anodic protection as opposed to cathodic protection). This method, for obvious reasons, would be extremely difficult to accomplish in chemical plant equipment.

It is, therefore, the primary object of this invention to provide alloys of titanium and alloys of chromium which are resistant to the attack of oxidizing and non-oxidizing corrosive media.

It is also an object of this invention to provide a method for increasing the resistance to non-oxidizing corrosive media of the metals titianum, chromium, and their alloys.

Other aims and advantages of this invention will be apparent from the following description and the appended claims.

In accordance with these objects a corrosion resistant alloy is provided consisting essentially of from 0.005 to 5 percent by weight in the aggregate of at least one metal selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum, gold, rhenium, and alloys thereof, and the balance a metal selected from the group consisting of titanium, chromium, and alloys thereof wherein said selected metal is present in predominant amounts.

It is believed that the important factor in obtaining the desired improvement, and the principle upon which the invention operates, lies in the production of sufficient local action current to anodically polarize the alloy into the passive region. High local action currents are created by high potential differences between the electrodes of the galvanic couple and by shallow polarization curve slopes. The current required to change the potential of either cathode or anode a given amount by polarization is proportional to the cathode and anode areas which, in turn, are determined by the noble metal content of the alloy.

Specific embodiments of alloys of the invention have been prepared and tested. Dramatic improvements in corrosion rates were obtained and are set forth in the following table in comparison with pure titanium and various titanium alloys. In these tests, the samples were degreased, pickled, dried, and weighed. They were then immersed in boiling acid of composition and concentration as set forth, for one period of 24 hours' duration, removed, washed, and weighed again. The corrosion rate was calculated and reported as mils penetration per year.

Table I indicates the results of noble metal additions to substantially pure titanium. Table II provides the same information as to noble metal additions to binary and tertiary titanium base alloys. The percentages given in each case are percentages by weight of the total alloy.

TABLE I

Effect of Noble Metal Additions on Corrosion Rate of Titanium

Composition, percent noble metal	Corrosion rate (mils/year)			
	Boiling H_2SO_4		Boiling HCl	
	1%	10%	3%	10%
Ti	455.3	2,952.6	241.8	4,479.7
Ti+0.01 Pt			9.0	1,411.8
Ti+0.37 Pt	1.3	39.0	1.0	71.2
Ti+2.00 Pt	1.0	36.0		
Ti+5.00 Pt		46.6		89.6
Ti+0.005 Pd			56.1	3,125.4
Ti+0.44 Pd	1.3	49.9	0.6	67.3
Ti+0.48 Au	3.2	206.4	8.7	145.5
Ti+0.60 Ir	Nil	44.8	2.6	87.6
Ti+0.48 Os	1.0	81.5	2.6	207.7
Ti+0.36 Re	8.7		29.0	
Ti+0.5 Rh	2.6	48.0	1.6	55.1
Ti+0.5 Ru	1.6	48.0	2.3	112.7

TABLE II

Effect of Noble Metal Additions on Corrosion Rate of Titanium Base Alloys

Composition, percent additive	Corrosion rate (mils/year)				
	Boiling H_2SO_4			Boiling HCl	
	10%	40%	55%	5%	20%
6 Al+4 V+Ti	5,520.0				
6 Al+4 V+Ti+0.1 Pd	767.0				
2.5 Al+15 V+Ti	3,280.0				
2.5 Al+15 V+Ti+0.1 Pd	379.0				
8 Mn+Ti	6,370.0				
8 Mn+Ti+0.1 Pd	261.0				
5 Mo+Ti				650	(1)
5 Mo+Ti+0.5 Pt				11	500
10 Mo+Ti				113	
10 Mo+Ti+0.2 Pd				9	300
15 Mo+1C+Ti		1,020		7	(1)
15 Mo+1C+Ti+0.2 Pd		100		14	194
20 Mo+Ti		56	2,190		133
20 Mo+Ti+0.05 Pd		12			39
20 Mo+Ti+0.1 Pd		12	53		41
20 Mo+Ti+0.2 Pd		8			38

Composition, percent additive	Corrosion rate (mils/year), boiling H_2SO_4, 10%
0.5 C+Ti	4,990
0.5 C+Ti+0.5 Pt	177
0.63 C+Ti	4,130
0.63 C+Ti+0.5 Pt	102
0.63 C+Ti+0.06 Pd	387
0.68 C+Ti+0.27 Pd	354
10 Cr+Ti	(1)
10 Cr+Ti+0.5 Pt	68
19.6 Cr+Ti+0.5 C	(1)
19.6 Cr+Ti+0.5 C+0.5 Pt	137
19.6 Cr+Ti+0.5 C+0.46 Pd	160

1 Dissolved

In the tables above, the corrosion rate of titanium, without any addition, is given first to serve as a comparison. It will be observed that all the noble metals tested were extremely effective in reducing the corrosion rate of both titanium and its alloys. It will be observed that as little as 0.005 percent by weight palladium produces a fourfold decrease in the corrosion rate of titanium in boiling 3.0 percent HCl. It will further be observed that, in general, additions of noble metals reduce the rate of corrosion of titanium and its alloys at least an order of magnitude, even in boiling non-oxidizing acids of concentrations as high as 55.0 percent.

The proportion of the noble metal addition may be varied according to the anticipated use. Where contact with more rigorous environments is anticipated, such as strong concentrations of acid, more noble metal is required. FIGS. 1 and 2 demonstrate the effectiveness of platinum and palladium in decreasing the rate of corrosion of titanium in hydrochloric and sulfuric acid, respectively. Referring to FIG. 1, whereas the addition of 0.035 percent palladium is effective in reducing the corrosion rate of titanium exposed to 10.0 percent boiling HCl to the level of approximately 100 mils penetration per year, only 0.005 percent is necessary to reduce the rate to the same level when titanium is exposed to 3.0 percent boiling HCl. Referring to FIG. 2 whereas the addition of 0.2 percent platinum is effective in reducing the corrosion rate of titanium exposed to 10 percent boiling H_2SO_4 to the level of approximately 50 mils penetration per year, only 0.015 percent is necessary to reduce the rate to the same level when titanium is exposed to 1 percent boiling H_2SO_4. For best results, in conditions where exposure to strong solutions is encountered, the additive is used in amounts of 0.1 to 0.5 percent. With amounts below 0.1 percent noble metal addition, the desired improvement in corrosion resistance may not be sufficient to meet the particular needs. As cited previously, as little as .005 percent of noble metal addition to titanium may suffice for low concentrations of acids. With amounts substantially in excess of about 2.0 percent, no marked degree of improvement results. The noble metals may be present in the alloy either singly or in any combination with each other.

The titanium-base alloys shown in Table II also exhibit improved corrosion resistance in non-oxidizing media when alloyed with one of the noble metals listed. It is seen from Table II that alloys containing at least about 80 percent by weight titanium are benefitted. Of especial significance is the titanium-molybdenum-noble metal alloy shown in Table II.

Some alloys of titanium and molybdenum are known to possess resistance to corrosive non-oxidizing media because of the resistance to such media naturally possessed by molybdenum. The resistance to non-oxidizing media of a titanium-40 percent molybdenum alloy is much greater than the resistance of pure titanium in such media. However, the increased resistance to non-oxidizing media poossessed by this alloy is acquired at the expense of the resistance to oxidizing media normally possessed by titanium. With amounts of less than 40 percent molybdenum in titanium, the resistance to non-oxidizing media is not as great. Below 15 percent molybdenum, a titanium molybdenum alloy shows little of this resistance to non-oxidizing media. However, by the addition to titanium-molybdenum alloys of one of the noble metals selected from the group ruthenium, rhodium, palladium, osmium, iridium, platinium, gold and rhenium, a corrosion resistance alloy is obtained that is suitable for use in both oxidizing and non-oxidizing media. The titanium-base alloy should contain from about 8 percent to 20 percent by weight molybdenum, and may contain up to 5 percent by weight of one or more of the noble metals. A preferred range of composition is from 8 to 20 percent molybdenum, from 0.05 to 2 percent palladium, and the balance titanium and incidental impurities. Any noble metal from the group listed above may be used; but because of economic considerations, it is preferred to use palladium.

For satisfactory commercial use an alloy may be prepared that consists of from 12 to 14 percent molybdenum, about 0.2 percent palladium, and the balance titanium and incidental impurities. The alloys shown in Table II include some high-molybdenum titanium-base alloys which show greatly improved resistance to non-oxidizing media, but do not exhibit the resistance to oxidizing media found in the alloys of this invention. For example, an alloy consisting of about 10 percent molybdenum, about 0.2 percent palladium, and the balance titanium will show about the same corrosion resistance in boiling 5 percent hydrochloricacid as titanium-20 percent molybdenum alloy; however, the low-molybdenum alloy of this invention has ten times greater resistance to an oxidizing environment, such as boiling 65 percent nitric acid, than the 20 percent molybdenum alloy.

TABLE III

Effect of Noble Metal Additions on Corrison Rate of Chromium

Nominal composition, percent noble metal	Corrosion rate (mils/year)								
	Boiling H_2SO_4							Boiling HCl	
	5%	10%	20%	30%	40%	50%6	0%	5%	10%
Cr	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)
Cr+0.1 Pt	1.8	1.0	7	22	103	335	(1)	0.7	14
Cr+0.5 Pt	0.5	2.7	9	28	175	143	37	0.42	
Cr+1.0 Pt			8					0.46	
Cr+2.0 Pt			10					0.42	
Cr+5.0 Pt			1.5					0.41	
Cr+0.5 Rh			2.8					0.68	
Cr+0.5 Os			64					16.0	
Cr+0.5 Pd		4.3						0.79	
Cr+0.5 Ru		5.1						0.84	
Cr+0.5 Ir		2.4						0.46	

1 Dissolved.

Table III indicates the results of noble metal additions to substantially pure chromium. Table IV provides the same information as to noble metal additions to binary and tertiary chromium-base alloys. The percentages given in each case are percentages by weight of the total alloy.

TABLE IV

Effect of Noble Metal Additions on Corrosion Rate of Chromium-Base Alloys

Nominal composition, percent noble metal	Corrosion rate (mils/year)					
	Boiling H_2SO_4				Boiling HCl	
	10%	20%	30%	40%	5%	10%
Cr+2 Cu	2,660	(1)	(1)	(1)	(1)	(1)
Cr+2 Cu+0.5 Pt	7	30	84	988	20	(1)
Cr+10 Mo	------	(1)	------	------	(1)	------
Cr+10 Mo+0.5 Pt	------	8	18	125	0.7	40
Cr+40 Fe+10 Mo	------	40	(1)	------	(1)	------
Cr+40 Fe+10 Mo+0.5 Pt	------	2	9	29	130	(1)

[1] Dissolved.

In Table III, the corrosion resistance of chromium without any addition is given first to serve as a comparison. Pure chromium, it will be noted, dissolves in both boiling sulfuric acid and boiling hydrochloric acid in the concentrations indicated. It will be observed that all the noble metals tested were extremely effective in reducing the corrosion rate of chromium. The degree of effectiveness varies with the quantity of noble metal added. It will be observed that as little as 0.1% by weight platinum renders chromium practically insoluble in 20% boiling sulfuric acid. Although the corrosion rate appears to increase with increasing amounts of platinum up to 5%, it will be understood that no significant difference actually exists between the various rates except for the 0.5 osmium rate. The 0.5 osmium addition, while it decreases the rate drastically, is not as effective as an equal amount of platinum. It will further be observed that, in general, additions of noble metal reduce the rate of corrosion of chromium in boiling non-oxidizing acids of concentrations as high as 60%. The proportion of noble metal addition may be varied according to the anticipated use. Where contact with a more rigorous environment is anticipated, such as strong concentrations of acid, more noble metal is required. For best results in conditions where exposure to strong solutions is encountered, the additive is used in amounts of between 0.05 and 0.5%. With amounts below 0.05% noble metal addition, the desired improvement in corrosion resistance may not be sufficient to meet the particular needs. As little as 0.005% of noble metal addition may suffice for low concentration of acid, however. With amounts substantially in excess of about 5%, no marked degree of improvement results. The noble metals may be present either singly or in combination with each other.

In Table IV, the corrosion rate of several chromium-base alloys, together with the rate of the same alloy with the platinum addition, is given for comparison. It will be seen that the base alloy readily dissolves in moderate to strong concentration of either sulfuric or hydrochloric acid. Although a chromium base alloy containing 40 percent iron and 10 percent molybdenum is able to withstand the lower concentrations higher than 20%. However, when only 0.5% platinum is added to the base alloy, a very marked decrease in the rate of corrosion results. The effectiveness of the noble metal addition, as before, depends on the strength of the corrosive medium and on the amount of noble metal added. Moreover, some alloys are more effectively protected by the same amount of noble metal addition than others. An 0.5% addition of platinum, for instance, while it decreases the rate of corrosion of a chromium-base alloy containing 2 percent Cu in 40 percent boiling sulfuric acid, is not as effective with this alloy as with a chromium-base alloy containing 10 percent molybdenum, or an alloy consisting of 40 percent iron, 10 percent molybdenum and the balance chromium. Additions of noble metals may also be made to chromium electrodeposit.

The alloys of the present invention may be prepared according to current metallurgical practice, although the invention is not limited by the method of preparation. The ingredients may be in any commercially pure form since the invention is not limited to the degree of its constituents.

The description of the invention above has been in terms of its specific embodiments. Modifications and equivalents will be apparent to those skilled in the art and this disclosure is intended to be illustrative of, but not necessarily to constitute a limitation upon, the scope of the invention.

This application is a continuation in part of my co-pending application Serial No. 732,793, filed May 5, 1958, now abandoned.

What is claimed is:

1. A corrosion-resistant alloy consisting essentially of from about 0.005 to about 5 percent by weight in the aggregate of at least one metal selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum, and rhenium, and the balance titanium and incidental impurities.

2. A corrosion-resistant alloy consisting essentially of from about 0.05 to about 2 percent by weight in the aggregate of at least one metal selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum, and rhenium, and the balance titanium and incidental impurities.

3. A corrosion-resistant alloy consisting essentially of about 0.05 percent by weight palladium, and the balance titanium and incidental impurities.

4. A corrosion-resistant alloy consisting essentially of about 0.05 percent by weight platinum, and the balance titanium and incidental impurities.

5. A corrosion resistant alloy consisting essentially of from about 8 to about 20 percent by weight molybdenum, from about 0.05 to about 2 percent by weight in the aggregate of at least one metal selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum, and rhenium, and the balance titanium and incidental impurities.

6. A corrosion-resistant alloy consisting essentially of from about 8 to about 20 percent by weight molybdenum, from about 0.05 to about 2 percent by weight palladium, and the balance titanium and incidental impurities.

7. A corrosion-resistant alloy consisting essentially of from about 12 to 14 percent by weight molybdenum, about 0.2 palladium, and the balance titanium and incidental impurities.

8. A corrosion-resistant alloy consisting essentially of about 0.2 percent by weight palladium, and the balance titanium and incidental impurities.

9. A corrosion-resistant alloy consisting essentially of from about 0.005 to about 5 percent by weight in the aggregate of at least one metal selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum, and rhenium, and the balance substantially all a metallic material selected from the group consisting of titanium and alloys of titanium with at least one element selected from the group consisting of aluminum, vanadium, manganese, molybdenum, and carbon containing at least about 80 percent by weight titanium.

10. A corrosion-resistant alloy consisting essentially of from about 0.05 to about 2 percent by weight in the aggregate of at least one metal selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum, and rhenium, and the balance substantially all a metallic material selected from the group consisting of titanium and alloys of titanium with at

least one element selected from the group consisting of aluminum, vanadium, manganese, molybdenum, and carbon containing at least about 80 percent by weight titanium.

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