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**ELECTROPOLISHING OF TITANIUM AND
TITANIUM ALLOYS**

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The present invention relates to the electrolytic treatment of metals, and in particular to improved methods and baths for electropolishing titanium and titanium base alloys.

In recent years, the increased commercial application of titanium has created a need for methods of treating titanium parts to obtain highly polished surfaces, and/or to obtain critical dimensional tolerances. Electropolishing baths comprising perchloric acid and acetic acid have been used by skilled technicians to polish relatively small titanium members such, for example, as metallographic specimens. However, as is well known in the art, baths comprising perchloric acid are extremely hazardous and numerous unexplained explosions have occurred during use thereof. As a result, industry has avoided the use of perchloric acid in the commercial type installations.

Even if the explosive hazard can be effectively controlled, and workers adequately assured as to the safety of the handling of baths comprising perchloric acid, such baths exhibit a number of other shortcomings which limit their general industrial application. The proportions of the bath are extremely critical from the standpoint of attaining useful electropolishing action. It is necessary to use such baths immediately upon preparation, and the life of such baths is rather short. Further, such critical formulation makes it difficult to reproduce the same electropolishing action from object to object.

There are a number of general requirements which must be met to bring about widespread commercial utilization of electrolytic baths for the electropolishing of titanium and base alloys thereof. Among these requirements are that the electropolishing bath provide good surface leveling, leaving clean and unfiled surfaces at the end of the treatment, have a wide operating range of current densities, be relatively insensitive to changes in the temperature of the bath, and be capable of operating at room temperature as well as over a range of temperatures normally encountered in most installations.

It is also desirable that the electrolytic baths be made up from inexpensive and easily obtainable commercial grade chemicals, be relatively easy to make up and have a comparatively long life.

Accordingly, the present invention is directed to improved methods and baths for electrochemically polishing objects of titanium and titanium base alloys, which baths are not hazardous to use and which are prepared from readily obtainable commercial grade materials.

The object of this invention is to provide an electrolyte for electrolytically bright polishing and/or levelling surfaces of members of titanium and titanium base alloys comprising sulfuric acid, fluoboric acid and hydrofluoric acid.

Another object of this invention is to provide a method for electrolytically bright polishing and/or leveling surfaces of members of titanium and titanium base alloys which comprises making the titanium member an electrode in an electrolyte comprising sulfuric acid, fluoboric acid and hydrofluoric acid and passing a current through said electrolyte of a sufficient density and for a sufficient period of time to effect a bright polish on the titanium member.

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Other objects of this invention will, in part, be obvious and will, in part, appear hereinafter.

For a better understanding of the nature and the objects of this invention, reference should be had to the following detailed description.

In accordance with this invention, it has been discovered that the surfaces of titanium and base alloys thereof can be electrolytically polished and/or leveled by means of a bath comprising sulfuric acid, fluoboric acid and hydrofluoric acid. It has also been discovered that additions of relatively small amounts of silicic acid to the above electrolyte will prevent etching of any valley areas that may be present on the surface of the metal.

The essential ingredients of the electrolytic bath of this invention are sulfuric acid, hydrogen fluoride gas and fluoboric acid. Based on 100% concentrations of these ingredients the bath will comprise, by weight, 100 parts by weight of 100% sulfuric acid, from about 3 to 8 parts of hydrogen fluoride gas, from about .6 part to 4.8 parts of 100% fluoboric acid and from about 15 to 35 parts of water. Additional water may be added if desired. If silicic acid is employed, it will be employed in an amount of from about .3 to .6 part by weight.

The bath employed in this invention is relatively easy to prepare, has a comparatively long life and is prepared from relatively inexpensive and easily obtainable commercial grade materials.

Concentrated sulfuric acid is employed in preparing the electrolytic bath, and is readily available commercially as a water solution containing from about 93% to about 98% of sulfuric acid.

As is known, hydrofluoric acid is obtainable commercially as a solution of hydrogen fluoride gas in water and is usually marketed in concentrations of from about 47% to about 53% of hydrogen fluoride gas.

Fluoboric acid is a colorless, clear, strongly acid liquid and may be employed as such in the electrolyte of this invention. However, it is available commercially as a 48% to 50% water solution thereof, and it is preferred to use this water solution of fluoboric acid in carrying out this invention.

Silicic acid is a white amorphous powder that is insoluble in water and most acids with the exception of hydrofluoric acid.

Since relatively large amounts of sulfuric acid are employed in preparing the electrolyte bath of this invention, accordingly, in formulating the electrolyte, it is preferred that the sulfuric acid be held constant and that the range of other ingredients employed be varied. These ingredients may be varied over a substantially wide range as indicated herein.

The electrolyte employed in this invention for electrolytically bright polishing titanium will comprise, by weight, 324 parts of 93% to 98% sulfuric acid, from about 19 parts to about 49 parts of 47% to 53% hydrofluoric acid, and from about 4 parts to 30 parts of 48% to 50% fluoboric acid. If silicic acid is employed in the above bath, it will be employed in an amount of from about 1 part to 2 parts by weight.

Water is present in the electrolyte as part of the commercially available ingredients employed in the preparation thereof. Small additional amounts of water may be added to the electrolytic baths if desired as an aid in controlling the proper current density. On the other hand, satisfactory electropolishing of the titanium workpiece can be obtained without the addition of any additional water other than that already present as above set forth in the preferred range of commercial ingredients.

Table I below sets forth illustrative electrolyte solu-

tion or bath formulations for electropolishing titanium in accordance with this invention:

TABLE I

Solution	Sulfuric Acid, Parts by Weight	Hydro-fluoric Acid, 52% Parts by Weight	Fluoboric Acid, 50% Parts by Weight	Silicic Acid, Parts by Weight
1-----	324	19.7	5.6	-----
2-----	324	19.7	5.6	1
3-----	324	26.7	5.6	-----
4-----	324	26.7	5.6	1
5-----	324	34.8	8.4	-----
6-----	324	45.8	8.4	1
7-----	324	41.8	25.2	-----
8-----	324	41.8	25.2	2
9-----	324	48.7	29.4	-----
10-----	324	48.7	29.4	1

In carrying out this invention, the titanium surface is preferably cleaned, either mechanically or with a solvent or both, to remove therefrom superficial impurities such as dirt, oil and grease. The surface is then made the anode in the electrolytic bath of this invention and direct current is applied and maintained until the desired brightening is effected. Any suitable material such as carbon may be employed as the cathode. The current density employed may vary. Current densities within the range of from about 10 to 80 amperes per square foot are satisfactory for the purposes of this invention with the optimum polishing and leveling characteristics being obtained within the relatively narrow range of from about 30 to 40 amperes per square foot. Agitation of the bath during electropolishing is recommended.

The temperatures of the bath will usually vary directly with the current density employed, but it is best to maintain temperatures below about 60° C. Temperatures of about 28° C. to about 30° C. are preferred as the electropolishing of the titanium surface is most efficient at these temperatures. Above about 60° C. it is noticed that there is more of a tendency for the surface of the titanium to become etched rather than to be bright polished.

Under the above conditions, satisfactory electropolishing of the surfaces of a titanium member will usually be accomplished within a period of time of from about 5 to 10 minutes.

The following example is illustrative of this invention:

Example 1

A welded spiral-wound titanium wire grid member for use in an electronic tube having undesired small weld splashes on the surface thereof is made the anode in a cell containing an electrolytic bath consisting of, by weight, 324 parts of 96% sulfuric acid, 34.8 parts of 52% hydrofluoric acid, 8.4 parts of 50% fluoboric acid and 1 part of silicic acid. A carbon cathode is employed as the other electrode in the bath. A current to provide a density of about 34 amperes per square foot is impressed on the titanium at a potential of about 7 volts for about ten minutes, the bath meanwhile being stirred mechanically. The temperature of the bath is maintained at about 30° C.

At the end of the operation the titanium member is quickly removed from the bath and rinsed in clean running water.

The weld splashes were no longer present on the surface of the titanium member and the member had a smooth highly-polished surface.

Examples of titanium base alloys that may be satisfactorily electropolished in the bath of this Example I in accordance with this invention are set forth in Table II below:

TABLE II

Alloy	Composition, Percent by Weight								
	C	O	N	Al	Cr	Fe	Mn	Mo	Ti
5	0.5	-----	-----	2	-----	2	-----	-----	Bal.
1	0.2	trace	trace	4	-----	trace	4	-----	Bal.
2	0.5	-----	-----	3	5	-----	-----	-----	Bal.
3	0.02	0.25	0.02	-----	2.7	1.3	-----	-----	Bal.
4	0.02	trace	0.02	-----	5	5	-----	5	Bal.
10	-----	-----	-----	-----	-----	-----	-----	-----	-----

The electrolytic bath of this invention and the method of this invention have been employed for large scale electropolishing of titanium members of complex geometries and these members have been satisfactorily bright polished by employing a potential of from about 3 to 10 volts.

There are no explosion hazards involved in the use of this bath and temperature control presents no substantial problem as good polishing is obtainable with temperatures ranging from room temperature to about 60° C. Furthermore, in polishing titanium surfaces in accordance with this invention, no oxide films are formed, which oxide films will usually lead to undesired etching and pitting of the titanium surface.

It is to be understood that the above description of this invention is illustrative and not in limitation thereof.

We claim as our invention:

1. An aqueous electrolyte for electrolytically bright polishing titanium and titanium base alloys consisting essentially of, by weight, 324 parts of sulfuric acid, from about 19 parts to 49 parts of hydrofluoric acid and from about 4 parts to 30 parts of 48% to 50% fluoboric acid.

2. An aqueous electrolyte for electrolytically bright polishing titanium and titanium base alloys consisting essentially of, by weight, 324 parts of sulfuric acid, from 19 to 49 parts of hydrofluoric acid, from 4 parts to 30 parts of 48% to 50% fluoboric acid and from 1 part to 2 parts of silicic acid.

3. The method of electrolytically polishing articles of titanium and titanium base alloys which comprises making the titanium article the anode in an aqueous electrolyte consisting essentially of, by weight, 324 parts of sulfuric acid, from about 19 parts to 49 parts of hydrofluoric acid, and from about 4 parts to 30 parts of 48% to 50% fluoboric acid and passing current therethrough of sufficient density and for a sufficient period of time to effect a polish on said titanium article.

4. The method of electrolytically polishing articles of titanium and base alloys thereof which comprises making the titanium article the anode in an aqueous electrolyte consisting essentially of, by weight, 324 parts of sulfuric acid, from 19 parts to 49 parts of hydrofluoric acid, from 4 parts to 30 parts of 48% to 50% fluoboric acid and from 1 part to 2 parts of silicic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,040,618	Mason	May 12, 1936
2,466,095	Gall	Apr. 5, 1949
2,542,779	Neill	Feb. 20, 1951
2,549,737	Weisner	Apr. 17, 1951
2,780,594	Dailey	Feb. 5, 1957
2,871,425	Burnham	Jan. 27, 1959

OTHER REFERENCES

Metallurgia, vol. 49, No. 295, May 1954, page 256.
Chemical Abstracts, vol. 48, 1954, pages 13,482 and 13,483.