This invention relates to the electropolishing of the refractory metals, especially columbium, though it is also applicable to tantalum, tungsten and molybdenum.

It is a primary object of the present invention to provide a method, and an electrolyte solution that can be used therewith, to electropolish the refractory metals in a manner particularly satisfactory for metallurgical work, which method is easy to perform; and effectively electropolishes in a matter of seconds; and that utilizes an electrolyte that is safe to handle and relatively inexpensive.

This and other objects are attained in accordance with my invention in which a solution composed of from 0.1 to 3 volume percent of 1.2 specific gravity (aqueous) hydrofluoric acid, and 2.5 to 7 volume percent of 1.8 specific gravity (aqueous) sulfuric acid and methanol is used under conditions hereinafter specified to electropolish columbium and the other refractory metals. By my method and electrolyte, I am able to electropolish the refractory metals very rapidly, i.e., within about 5 to 30 seconds, and produce a surface that is fully satisfactory for purposes of metallographic work.

The total acid concentration in the electrolytic solution of the invention ranges from a minimum, on a volume basis, of 3.75 percent with a minimum sulfuric to hydrofluoric acid ratio of 2:1, to a maximum of approximately 7.5 percent with a maximum sulfuric acid to hydrofluoric acid ratio of 12:1, with the balance being methanol. It is to be noted that the range of acid concentrations specified is necessary to secure satisfactory results, though the actual acids used can be of a different concentration from that stated, for equivalent quantity-concentration combinations can be used if desired.

Electropolishing is accomplished in accordance with the invention while using current densities within the range of 25 to 60 amperes per square inch and using from 50 to 90 volts across the cell. Within these ranges the higher current densities and voltages are used with shorter times and conversely the lower current densities and voltages with longer times.

In operation, it has been found essential to maintain the electrolytic solution at room temperature or below, i.e., not exceeding about 70° F., to prevent the formation of an anodic film. This temperature can readily be maintained by using a full flowing electrolyte, which serves to carry away heat from the work surface. Also, conventional cooling means externally of the cell can be used, if desired, to be sure that the requisite low electrolyte temperature is maintained.

The invention will be readily understood upon considering the following example in which the details are given by way of illustration and not by way of limitation.

An electrolyte solution composed of 5 volume percent of sulfuric acid (1.84 specific gravity), 0.4 volume percent of hydrofluoric acid (1.2 specific gravity), and the remainder methanol was prepared by adding the acids to a container that had the methanol in it. A strip of columbium, prepared by mechanically polishing its surface through 3/0 metallographic paper, was made the anode in a commercially available polishing cell comprising a D.C. source of current and a stainless steel cathode. The current was then adjusted to provide a current density of 35 amperes per square inch of the columbium strip at 55 volts. After 15 seconds of operation, the power was turned off and the columbium strip was examined. The surface was found to be essentially bright and smooth, there being no evidence of pitting or coarseness at magnifications as low as 100X.

Similar results in very short times have been obtained on tantalum strip, tungsten bar stock and as-cast specimens of molybdenum. Through experience, the following ranges of electrolyte composition, current density, voltages and time of treatment have been determined to constitute the preferred ranges for the respective refractory metals indicated.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Volume percent</th>
<th>Columbium Strip</th>
<th>Tantalum Strip</th>
<th>Molybdenum as-cast</th>
<th>Tungsten Bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>HF</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Current Density, Amp./in.²</td>
<td>30 to 50</td>
<td>30 to 50</td>
<td>30 to 50</td>
<td>30 to 50</td>
<td></td>
</tr>
<tr>
<td>Voltage, volts</td>
<td>50 to 60</td>
<td>50 to 60</td>
<td>50 to 60</td>
<td>50 to 60</td>
<td></td>
</tr>
<tr>
<td>Time, seconds</td>
<td>10 to 20</td>
<td>10 to 20</td>
<td>10 to 20</td>
<td>10 to 20</td>
<td></td>
</tr>
</tbody>
</table>

It is particularly noteworthy that the electrolytic solutions of this invention are relatively weak acid solutions compared to those shown in prior art. This is advantageous because my electrolyte is relatively non-corrosive, is safe to handle and considerably less expensive than the more concentrated solutions. The solution concentration is also truly surprising when one compares the operating times (a few seconds) of my process with those of the prior art (many minutes). It is further surprising when it is observed that there was no known solution, prior to the present invention, for electropolishing columbium. It may have been thought that a very concentrated acid would be essential for treating columbium; but my discovery is directly opposed to that conclusion.

From the foregoing data and discussion, it is evident that the present invention provides a ready solution to the problem of electropolishing the refractory metals. Electropolishing procedures for molybdenum, tantalum and tungsten have been proposed heretofore, but experience with them has demonstrated their unsuitability as measured by surface inspection under low magnification. While my invention is primarily directed to providing the art with a procedure for electropolishing columbium, it is also effective for the other named refractory metals with the advantages already stated.

It will be appreciated by those skilled in the art that variations from the details given can be made. Other cathode materials can be used such, for example, as carbon or other material. Further, in preparing surfaces for electropolishing, they must first be mechanically polished through the 3/0 metallographic paper. Polishing through the 4/0 paper or further can also be used where the condition of the specimen warrants it.

In accordance with the provisions of the patent statutes, I have described my invention and set forth what is now believed to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention can be practiced otherwise than as specifically described.

I claim:
1. The method of electropolishing a refractory metal selected from the group consisting of columbium, tantalum, molybdenum and tungsten including the steps of making said refractory metal the anode in an electrolytic solution consisting essentially of hydrofluoric acid, sulfuric acid and methanol wherein the total acid concentration in said solution ranges, on a volume basis, from a minimum of 3.75 percent with a minimum sulfuric acid to hydrofluoric acid ratio of 2 to 1 to a maximum of
about 7.5 percent with a maximum ratio of sulfuric acid to hydrofluoric acid of 12 to 1.

2. The method of electropolishing columbium including the step of making a part composed of columbium the anode in an electrolytic solution consisting essentially of 0.1 to 3 volume percent of 1.2 specific gravity hydrofluoric acid, 2.5 to 7 volume percent of 1.84 specific gravity sulfuric acid and the remainder methanol, with the acids being used in ratios to provide a total acid concentration within the range of about 3.75 percent to 7.5 volume percent.

3. A method according to claim 2 in which said columbium is in the form of a strip and current is passed through said electrolytic solution to provide a current density at said strip of about 30 to 35 amperes per square inch.

4. A method in accordance with claim 1 in which said refractory metal is tantalum and it is subjected to current for a period of time of about 8 to 25 seconds at a current density of about 30 to 35 amperes per square inch.

5. A process in accordance with claim 1 in which said refractory metal part is an as-cast molybdenum bar, and current is passed through said electrolyte for 6 to 12 seconds at a current density of about 35 to 45 amperes per square inch.

6. A method in accordance with claim 1 in which said refractory metal part is tungsten bar, and current is passed through said electrolyte for about 8 to 15 seconds at a current density on the order of 30 amperes per square inch.

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