JUL 6 1965

CONF-650414-3

MASTER

A "Universal" Electropolishing Method*

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ABSTRACT

An electrolytic polishing method utilizing a low temperature perchloric acid-methanol electrolyte has been developed. Over fifty metals have been successfully polished with this method. Examples of voltage current-density curves are given and photomicrography of both optical and transmission electron microscopes examples are shown.

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*Work was performed at the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1746.

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Introduction

Since Jacquet's first experiments with electropolishing many solutions and methods have been found which are successful with specific metals and alloys. Several excellent reviews of electropolishing theory and methods have been written^{1, 2,} from which the reader may obtain information concerning these methods. Previously two of the present authors investigated the electropolishing of the rare earths³ and were successful with a rather dilute perchloric acid-methanol solution at low temperatures. Those results stimulated the present investigation to determine the possibilities of producing an electropolishing method which would be useful for most metals and alloys. This paper will describe this investigation and the successful results. With recent developments in the use of transmission electron microscopy to investigate the structure of metals and the success of electropolishing thinning methods, there has been a number of investigations to determine the best and most efficient electropolishing method for producing thin foils. The advent of transmission electron microscopy has broadened the interests of metallurgists and physicists to include all of the metals which can be successfully thinned for examination. With a great variety of specimens, the need for a single electropolishing with a wide range solution of suitability for electrothinning is apparent. In addition, analytical chemists are often plagued by the difficulty of placing some metals in solution so that quantitative analysis can be accurately and simply performed. An electrolytic dissolution method might be useful

and desirable in analytical applications. The mechanisms of electropolishing have been studied by several investigators^{4, 5, 6} and several models have emerged. The verification of a model or perhaps the development of a new model may be enhanced by the ability to compare electropolishing results among many metals with the only unique variable being the metal.

Experimental Procedure

A Buehler electropolisher was used for all experiments described in this investigation. The amperage was measured with an auxillary ammeter which could be read accurately to 0.001 ampere. The cathodes were made of austenitic stainless steel in the form of 5.5 cm diameter x 0.2 cm. thick sheet with a 13.8 cm long x 0.4 cm diameter stem. The cathode was inserted so that the flat portion became the false bottom for a 250 ml Pyrex beaker. The stem of the cathode extended above the top of the beaker and provided the connection to the cathode leads. The specimen to be electropolished was the anode. The solution compositions were all made up by volume with 70% perchloric acid. The perchloric acid should always be added to the methanol with moderate stirring during the addition. There is no evidence that these solutions are hazardous but, in keeping with good general safety practice, the solutions are made up as required and discarded at the end of each day. The beakers, after being filled with the electrolyte, were placed in a dry ice-acetone mixture which was contained in an insulated pyrex glass beaker 8 cm deep x 15 diameter. This permitted the temperature of the electrolyte to be maintained at temperatures down to -76°C . Temperatures of the electrolyte were measured with a toluol thermometer. The temperature of the specimen surface was measured with a chromel-alumel thermocouple which was inserted in a hole filled with Woods metal in the side of the anode and covered with insulating lacquer.

The specimens to be electropolished were coated on all edges by an insulating lacquer to prevent edge polishing and to control area

size. The specimens were gripped at one edge with stainless steel tweezers which were also coated with lacquer. After allowing the lacquer to dry the specimen was immersed completely in the cold electrolyte and allowed to cool for several minutes. After electropolishing the specimens are removed from the electrolyte with the current on and quickly immersed and vigorously agitated in an ethanol wash bath. After a few seconds, the specimen was agitated in a clean ethanol bath. This procedure was continued through several baths to insure complete removal of the acid electrolyte. If improperly cleaned, the specimen tended to oxidize. Finally the specimen was dried in a gentle stream of warm air and examined.

Results

Preliminary results indicated that different metals gave similar current density-voltage behavior during electropolishing. Therefore one metal, cobalt, was selected for detailed study of the electropolishing variables. An anode area of 0.4 square centimeters was chosen as a convenient size for most of the electropolishing experiments. Figures 1 and 2 show the current density versus voltage curves at -70°C for 6% and 1% perchloric acid solutions. A plateau was observed on the 6% solution curve which was very flat and comparable with curves observed in the phosphoric acid type electrolytes. The polish occurring on this plateau is excellent and results are comparable at different voltages on the plateau. Polishing at voltages above 50 volts on this area produces surfaces with considerable relief although in general the macro appearance was bright and highly reflective. In Fig. 2 a current density vs voltage curve using a 1% perchloric acid-methanol solution is illustrated. A plateau was observed between 15 and 30 volts but it was not as flat as the plateau observed with 6% solution. The polishing action on this plateau is indistinguishable from that obtained using the 6% mixture. An advantage of the 1% solution is that the decrease in speed of metal removal makes the electrothinning process easier to control. A study was made of electropolishing at 25°C with identical specimens in these two solutions. The current density voltage curves, shown in figure 3 did not exhibit a plateau. There was a continual

increase in the temperature of the electropolishing solution in the 6% solution and the current density continued to increase with time at each voltage. The current densities given in Figure 3 were after 2 minutes of electropolishing. In the 1% solution there was no significant temperature rise and the results were steady values. The polish obtained at this temperature was very poor and there was an insoluble layer on the surface of the cobalt. It should be noted that some specimens certainly can be electropolished without difficulty at 25°C, with aluminum being a noteworthy example, but that many metals can not. The absence of a plateau at 25°C is perhaps not unexpected when it is considered that the current densities even at low voltages are well above those observed in these solutions at lower temperatures.

During the course of this investigation it was observed that stirring of the solution was not necessary and for some materials such as niobium stirring was detrimental to good polishing. Figure 4 shows the effects of stirring a 1% perchloric acid-methanol mixture on current density-voltage curves. The unstirred solution has a lower current density value on the plateau but has a much better defined plateau than the stirred solution. If electropolishing is a diffusion-controlled process this may very well be expected provided other variables such as heat generation are not interfering.

The throwing power of an electrolytic solution is usually enhanced by the addition of water to the electrolyte. Figure 5 shows the result of adding 5% water to the 1% perchloric acid-methanol solution. The current density is lowered at identical voltages but the plateau has

a similar shape. Many metals could be chemically etched after electropolishing in the same solution simply by decreasing the voltage to zero. The addition of water did not appear to change the polishing effects but was essential in achieving uniform and reproduceable etching. If etching is to be done the water should be added to the solution before polishing.

The current density at constant voltage varied with time even when there was no temperature rise in the solution. Figures 6 and 7 show current density vs time curves. In both the 1% solution and the 6% solution there is quite a low resistance initially followed by a rather rapid increase in resistance. Furthermore, the 6% solution requires at least 30 seconds to arrive at a steady value whereas the 1% solution requires only 18 seconds. This difference would indicate that the electropolishing mechanism proceeded by diffusions since it should take longer for the anions to be consumed at the surface of the anode in the 6% than in the 1% solution and should thus require more time for steady rate conditions to be attained.

Most of the metals of which samples could be obtained were tested in these solutions. Generally, the investigation was only followed far enough to establish whether or not electropolishing was occurring. The optimum conditions for polishing were not determined in every case.

Fig. 8 is a chart showing the metals in a periodic chart arrangement and indicating these which have been electropolished by this technique. Of those metals which were tried, only platinum and thallium were not polished successfully. Many of the metals were also thinned for transmission electron microscopy in the same solutions. When platinum was polished at low temperatures in a 6% perchloric acid-

methanol solution to which 10% hydrochloric acid had been added, the solution showed an increasingly darker green coloration. This possibly indicates the solution of platinum at the anode but after times as long as eight hours no observable effects on the surface were seen. Probably the platinum is polishing but at a very slow rate. From the similarity of their properties one would expect osmium and iridium to polish very slowly. Electropolishing of thallium was unsuccessful because of a thick insoluble layer which could not be removed from the surface. Gold will polish in the low temperature perchloric-acid-methanol mixture but will polish more evenly if 5% hydrofluoric acid is added to the electrolyte. The successful polishing of tantalum requires the use of hydrofluoric acid in the electrolyte. Many of the other untried metals such as the alkali metals could probably be electropolished but the difficulty in handling these metals without special precautions has discouraged attempts to polish these materials. Bismuth has been polished in these low temperature solutions but they are not recommended for general use because of the danger of forming an explosive surface layer reported by Tegart.¹

Photographs illustrating results which have been obtained with the low temperature techniques are shown in Figures 9 through 18. Each metal is depicted in both an optical photomicrograph and a transmission electron microscope image. Lead was probably the most difficult so far as transmission microscopy was concerned because of its high density and difficulty in handling the thin foils due to the softness of lead at room

temperature. There was no difficulty in polishing of any of these metals.

Conclusions

With the ability to polish at least 50 different metals the term "universal method" can perhaps be aptly applied. The only metals which at the present time are not readily polished by this method are the highly oxidation resistant metals. This is not unexpected because from an oxidation mechanism consideration these metals would not electropolish easily. There is some indication that the platinum metals will electropolish as shown by the change of color in the solution but the times for polishing are probably excessive. An additional limitation is that some changes in structure may occur at the low temperatures used in this procedure and in these cases this method would not be applicable.

The danger which can be encountered in the perchloric acid-acetic anhydride solvent solutions have been thoroughly discussed by Heyes⁷. The solutions used in this study are much more dilute and would not be expected to have explosive characteristics.

With the availability of a single "universal" polishing solution, a determination of the mechanism of electropolishing is now more feasible than in the past. Particularly, the troublesome aspects of the present method may, when explained satisfactorily, provide important clues to the polishing mechanism.

Acknowledgements

The authors would like to express their gratitude to Dr. T. Scott for the many helpful discussions during the course of this investigation. Thanks are due to Mr. C. Owen and L. Reed for the rolling of the metals and Dr. O. N. Carlson and his group for the melting of some of the metals.

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

X 250

1 μ |-----|

LANTHANUM

HClO_4 -- Methanol Electrolyte

Temperature: -70°C

Fig. 9

X 250

1 μ

MAGNESIUM

HClO_4 -- Methanol Electrolyte

Temperature: -70°C

Fig. 10

X 250

1 μ

COBALT

HClO_4 -- Methanol Electrolyte

Temperature: -70°C

Fig. 11

X 250

1 μ

ZIRCONIUM

HClO_4 -- Methanol Electrolyte

Temperature: -70°C

Fig. 12

X 250

1 μ

NIOBIUM

HClO_4 -- Methanol Electrolyte

Temperature: -70°C

Fig. 13

X 250

1 μ

TIN

HClO_4 -- Methanol Electrolyte
Temperature: -70°C

Fig. 14

X 250

1 μ

LEAD

HClO_4 -- Methanol Electrolyte

Temperature: -70°C

Fig. 15

X 250

1 μ

STEEL

HClO_4 -- Methanol Electrolyte

Temperature: -70°C

Fig. 16

X 250

1 μ

ALUMINUM

HClO_4 -- Methanol Electrolyte

Temperature: -70°C

Fig. 17

X 250

1 μ

URANIUM

HClO_4 -- Methanol Electrolyte

Temperature: -70°C

Fig. 18