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BERYLLIUM-COPPER ELECTROPOLISHING SOLUTION

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8 Claims

ABSTRACT OF THE DISCLOSURE

An aqueous electrolyte for leveling and polishing a beryllium-copper surface, said electrolyte comprising phosphoric acid, chromic acid, a maximum of 44 ml./liter of sulfuric acid, 12 to 22 ml./liter of fluoboric acid and a maximum of 22 ml./liter of hydrofluoric acid.

BACKGROUND OF THE INVENTION

The invention herein described was made in the course of and under a contract, or subcontract thereunder, with the United States Strategic Systems Projects Office, Department of the Navy.

This invention relates generally to electrochemical baths for processing beryllium-copper material and is concerned more particularly with an electrolytic solution for leveling and polishing the surface of a continuous beryllium-copper wire.

Generally, a magnetic memory wire comprises a length of beryllium-copper wire which has been plated with copper and then coated with a thin film of permalloy. In order to obtain a durable copper plating and a consistent coating of permalloy, the wire substrate must have a uniform diameter and a very smooth surface finish. However, commercially available wire usually has surface defects, such as scratches, for example, which occur frequently along the surfaces of the wire, as a result of the drawing and annealing processes used in producing the wire. Consequently, a number of methods have been developed for treating the surface of commercially procured wire to obtain beryllium-copper wire of the desired quality for magnetic memory plating. One method of providing wire with a uniform diameter and a smooth surface finish comprises the steps of etching the high spots off the wire in a chemical etching bath and polishing the leveled surface of the wire to a smooth finish in an electropolishing bath. To avoid subsequent degradation of the processed wire surface, the wire is usually copper plated and permalloy coated immediately after the leveling and polishing operations are completed. For this reason, the etching bath and the electropolishing bath generally are incorporated directly into a magnetic plating line.

Typically, a magnetic plating line comprises a linear array of chemical cells in spaced, parallel relationship with one another. At one end of the line, a spool of wire, usually beryllium-copper, is rotatably mounted in colinear, spaced relationship with the array of cells. In operation, wire feeds continuously off the spool and is drawn longitudinally through the linear array of chemical cells. Generally, one of the cells in the array contains a pool of conductive liquid, such as mercury, for example, whereby electrical connections are made to the continuously moving wire, for electrochemical purposes. As the wire passes longitudinally through the linear array of cells, the surface of the wire is cleaned, processed and rinsed in the initial cells, copper plated in the intermediate cells and permalloy coated in the final cells of the array. Generally, two of the initial cells in the linear array are the aforementioned etching and electropolishing baths for leveling and polishing the wire surface respectively.

In the etching bath, the surface of the wire is leveled

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by the solution in the bath acting chemically on the material of the wire. In the electropolishing bath, the wire is connected electrically as the anode of an electrolytic cell and passes longitudinally through a hollow cylinder of thin, metallic material, such as platinum, for example, which is the cathode of the cell. The cathode cylinder is immersed in an electrolytic solution which removes ions from the surface of the wire and plates them on the surrounding cathode surface. In this manner, the leveled surface of the wire is microscopically polished to a very smooth finish. However, since the wire is traveling longitudinally through the etching and electropolishing baths at plating line velocity, each discrete length of the wire is exposed to the respective leveling and polishing actions of the etching and electropolishing baths only while traversing the respective baths. When the velocity of the magnetic plating line is increased, each discrete length of the wire will traverse the respective etching and electropolishing cells in correspondingly shorter intervals of time. Consequently, the etching and electropolishing solutions must be capable of leveling and polishing each discrete length of wire surface at a rate which is compatible with the expected velocity range of the magnetic plating line.

SUMMARY OF THE INVENTION

Accordingly, this invention provides an aqueous electrolyte for an electropolishing bath which both levels and polishes the surface of a beryllium-copper wire while the wire is moving longitudinally through the bath at plating line speeds up to twenty-five inches per minute. With this bath in a magnetic plating line a preceding chemical etching stage is not required for leveling the wire surface before the electropolishing operation is initiated. The inventive electrolyte comprises 800–900 ml./liter of phosphoric acid, 30–50 gm./liter of chromic acid, 36–44 ml./liter of sulphuric acid, 12–22 ml./liter of fluoboric acid and a balance of distilled water. The activity of the inventive electrolytic solution can be accelerated to operate satisfactorily on a beryllium-copper wire moving longitudinally through the solution at plating line speeds between twenty-five and forty inches per minute by adding 12–22 ml./liter of hydrofluoric acid to the solution and reducing the balances of distilled water correspondingly.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The inventive electrolytic solution was evaluated in an electropolishing cell of a typical magnetic plating line. However, when it was determined that sufficient leveling action took place in the electropolishing cell having the inventive electrolytic solution therein, the preceding chemical etching cell was removed from the magnetic plating line. Consequently, the results obtained during this evaluation study were achieved without having a chemical etching cell in the magnetic plating line. The wire used for evaluating the inventive electrolytic solution was a commercial grade, No. 125, beryllium-copper wire which had been drawn to 5.5 mils diameter and had a surface finish of sixteen microinches. The electropolishing cell used for evaluation of the inventive electrolytic solution was nine inches long and the associated plating line was operated at various speeds up to fifty inches per minute. The composition of the electrolyte and operating parameters for the electrolytic bath are as follows:

85% (AR grade) Ortho-phosphoric acid—800–900 ml./liter
Chromic acid—30–50 gm./liter
98% (AR grade) sulfuric acid—36–44 ml./liter
48% (AR grade) fluoboric acid—12–22 ml./liter
Distilled water—balance
Operating temperature—30° C.–50° C.
Current density—2–10 amps./sq. in.

Evaluation studies indicated that, in the above electrolytic solution, phosphoric acid acts as the polishing medium and chromic acid functions as a depitting agent. However, without sulfuric acid in the above electrolyte, pitting still may occur as a result of small traces of cobalt material in the surface of the beryllium-copper wire. Investigation disclosed that the percentage composition of commercial grade, beryllium-copper wire generally includes a small percentage of cobalt, such as four-tenths of one percent, for example. This cobalt material may occur in the form of minute "cobalt rich" areas along the surface of the beryllium-copper wire. When sulfuric acid is omitted from the above electrolyte, the resulting electrolytic solution selectively etches these cobalt rich areas at a faster rate than the surrounding beryllium-copper material. As a result, the surface of the surface of the wire becomes pitted and unacceptable for subsequent copper plating and permalloy coating. However, when sulfuric acid is present in the above electrolyte, within the concentration range specified, the beryllium-copper material is etched uniformly with the cobalt material and pitting is avoided. On the other hand, when the beryllium-copper material does not include traces of cobalt material, the sulfuric acid still etches the beryllium-copper material at a uniform rate. Thus, the sulfuric acid stabilizes the etching rate of the above electrolyte and aids in leveling the surface of the wire to a uniform diameter. However, it has been determined empirically that if the concentration of sulfuric acid exceeds the specified maximum value, the etching action of the resulting electrolyte will exceed the polishing action of the electrolytic bath. As a result, the surface of the beryllium-copper wire will not have the high degree of smoothness required for magnetically plated memory wire. Therefore, the upper limit specified for the concentration of sulfuric acid in the above electrolyte is critical.

It has been determined also that the concentration range specified for fluoboric acid, in the above electrolyte, is critical at both the upper and lower limits. When the concentration of fluoboric acid is below the specified minimum value, ionic material from the surface of the beryllium-copper wire plates very poorly on the cathode of the electrolytic bath. Consequently, a mossy coating forms on the cathode; and, eventually, some of the plated material falls back into the electrolytic solution. As a result, a sludge forms in the electrolyte which clogs the orifices of the electrolytic cell and reduces the effective life of the bath. However, when the concentration of fluoboric acid is within the specified limits, a smooth, tightly adherent plating forms on the cathode and the conductivity of the bath is increased. As a result, excess sludge is avoided and the effective life of the bath is prolonged. On the other hand, when the concentration of fluoboric acid exceeds the specified maximum value, the etching action of the resulting electrolytic solution exceeds the polishing action of the electrolytic bath. Consequently, the surface of the wire will not have the high degree of smoothness required for magnetically plated memory wire. Thus, the fluoboric acid, when present in the above electrolyte within the specified critical limits of concentration, stabilizes the etching action of the electrolytic solution and promotes a tightly adherent cathode plating.

With the above electrolyte in the aforementioned electropolishing cell of the magnetic plating line, acceptable magnetic memory wire was obtained at plating line velocities up to and including twenty-five inches per minute. As stated previously, it was found that this inventive electrolyte will both level and polish a beryllium-copper wire satisfactorily without the aid of a prior chemical etching stage in the magnetic plating line. Evaluation tests disclosed that the described electrolyte will reduce a 5.5 mil diameter beryllium-copper wire to a uniform $4.9 \pm .15$ mil diameter and polish the leveled surface of the wire to a finish of four microinches or better. Thus, by means of the electrochemical treatment provided by this inven-

tive electrolyte, commercial grade beryllium-copper wire can be reprocessed to obtain wire having the uniformity and smoothness required for subsequent magnetic plating.

At plating line velocities in excess of twenty-five inches per minute, however, the yield of acceptable memory wire drops off significantly. Rejectable lengths of wire occur at more frequent intervals and become increasingly longer as the velocity of the magnetic plating line is increased. Investigation disclosed that, at plating line velocities greater than twenty-five inches per minute, the above electrolyte acts too slowly to completely process each discrete length of the wire passing through the bath in correspondingly shorter intervals of time. Attempts were made to accelerate the electrochemical activity of the above electrolyte by increasing the respective concentrations of sulfuric acid and fluoboric acid. However, as pointed out earlier, when the concentration of sulfuric acid or fluoboric acid exceeds the respective maximum values, specified above, the etching action of the resulting electrolytic solution increases faster than the polishing action and the surface of the wire becomes degraded. Experimental tests revealed that adding a small amount of hydrofluoric acid to the above electrolyte would produce corresponding increases in both the leveling and polishing actions of the electrolytic solution. In this manner, the etching and polishing actions of the above electrolyte can be maintained in balance while the electrochemical activity of the bath is increased to a processing rate compatible with magnetic plating line velocities in excess of twenty-five inches per minute. The resulting composition of the electrolyte, thus modified, and the associated operating parameters of the electrolytic bath are as follows:

85% (AR grade) ortho-phosphoric acid—80-900 ml./liter
 Chromic acid—30-50 gm./liter
 98% (AR grade) sulfuric acid—36-44 ml./liter
 48% (AR grade) fluoboric acid—12-22 ml./liter
 48% (AR grade) hydrofluoric acid—12-22 ml./liter
 Distilled water—balance
 Operating temperature—30° C.-50° C.
 Current density—2-10 amps/sq. in.

With this second electrolyte in the aforementioned electropolishing cell of the magnetic plating line, acceptable magnetic memory wire was obtained at plating line velocities between twenty-five and forty inches per minute. At plating line velocities below twenty-five inches per minute the diameter of the wire is reduced excessively and becomes unacceptable as magnetic memory wire. At plating line velocities above forty inches per minute, the yield of acceptable memory wire drops off considerably. Attempts to accelerate the electrochemical activity of this second electrolyte by increasing the concentration of hydrofluoric acid above the specified maximum value, results in the etching rate of the resulting electrolytic solution increasing faster than the polishing rate of the solution. As a result, the surface of the wire will not have the high degree of smoothness required for magnetically plated memory wire. Therefore, the upper limit specified for the concentration of hydrofluoric acid in this second electrolyte is critical.

Thus, there has been disclosed herein an electrolyte for leveling and polishing the surface of a beryllium-copper wire while the wire is moving longitudinally through the electrolyte at plating line velocities equal to or less than twenty-five inches per minute. There also has been disclosed herein a second electrolyte for leveling and polishing the surface of a beryllium-copper wire while the wire is moving longitudinally through the second electrolyte at plating line velocities between twenty-five and forty inches per minute. From the foregoing, it will be apparent that various changes may be made by those skilled in the art without departing from the spirit of this invention as expressed in the appended claims. It is to be understood, therefore, that all matter described

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herein is to be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. An aqueous electrolyte for leveling and polishing beryllium-copper material, said electrolyte comprising phosphoric acid, a metal compound, a maximum of 44 ml./liter of 98 percent sulfuric acid and a maximum of 22 ml./liter of 48 percent fluoboric acid.
2. An aqueous electrolyte as set forth in claim 1 wherein said electrolyte includes a maximum of 22 ml./liter of 48 percent hydrofluoric acid.
3. An aqueous electrolyte as set forth in claim 1 wherein said electrolyte comprises a maximum of 900 ml./liter of 85 percent ortho-phosphoric acid, a maximum of 50 gm./liter of chromic acid, a maximum of 44 ml./liter of 98 percent sulfuric acid and 12 to 22 ml./liter of 48 percent fluoboric acid.
4. An aqueous electrolyte as set forth in claim 3 wherein said electrolyte includes a maximum of 22 ml./liter of 48 percent hydrofluoric acid.
5. An aqueous electrolyte as set forth in claim 3 wherein said electrolyte comprises 800-900 ml./liter of 85 percent orthophosphoric acid, 30-50 gm./liter of chromic acid, 36-44 ml./liter of 98 percent sulfuric acid and 12-22 ml./liter of 48 percent fluoboric acid.
6. An aqueous electrolyte as set forth in claim 5 wherein said electrolyte includes 12-22 ml./liter of 48 percent hydrofluoric acid.
7. A method for leveling and polishing the surface of a beryllium-copper wire comprising connecting the wire electrically as the anode of an electrolytic cell, said cell having a length equivalent to nine inches and an electrolyte therein including phosphoric acid, chromic acid, a

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maximum of 44 ml./liter of 98 percent sulfuric acid and 12-22 ml./liter of 48 percent fluoboric acid; maintaining the temperature of the electrolyte at 30-50° C.; passing a current density through the cell of 2-10 amperes per square inch and moving the wire longitudinally through the cell at a velocity no greater than twenty-five inches per minute or the equivalent thereof.

8. A method as set forth in claim 7 wherein said electrolyte includes a maximum of 22 ml./liter of 48 percent hydrofluoric acid and said wire moves longitudinally through the cell at a velocity of 25-40 inches per minute or the equivalent thereof.

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