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3,560,356

PROCESS OF ELECTROLYTIC PICKLING OF COPPER-BERYLLIUM ALLOYS

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No Drawing. Filed May 19, 1967, Ser. No. 639,608

Claims priority, application France, June 10, 1966, 64,929

Int. Cl. C23b 1/00

U.S. Cl. 204—141

7 Claims

ABSTRACT OF THE DISCLOSURE

A process for pickling parts formed of copper-beryllium alloy in which small amounts of nickel or cobalt may be present as additional alloying elements, wherein the part to be pickled is connected to the anode in a direct current electrolysis cell in which the electrolyte is an aqueous solution of an alkali metal halide present in an amount within the range of 100–200 grams per liter and a surface active agent.

This invention relates to the process for pickling beryllium containing copper alloys and it relates not only to copper alloys containing 1.8–2% beryllium but also to such alloys which may contain small amounts of nickel and/or cobalt and to ternary alloys containing 0.4 to 0.7% beryllium, 1.2–2.5% nickel or 2.3 to 2.7% cobalt.

Semifinished products, sheets, strips, wires and the like which are formed of such alloys are usually subjected to thermal treatments whereby an oxide layer forms on the surfaces, notwithstanding the precautions which might be taken to avoid surface oxidation. Elimination of such oxide layer is difficult and removal is effected by a pickling operation.

Pickling becomes increasingly difficult at increasing temperature. It is for this reason that it is difficult to pickle ternary alloys of the types described having a relatively high cobalt or nickel content by introduction into a pickling solution at a temperature of about 900° C.

Two techniques are employed generally for pickling copper-beryllium alloys. In one system, pickling is carried out in an aqueous solution containing 20–50% by volume sulphuric acid. The operation is carried out at a temperature within the range of 40–60° C. by immersion for 10–60 minutes, depending somewhat on the degree of oxidation. After rinsing with water, the part is immersed for a few seconds in a chromatosulphuric mixture containing 50 g. chromic acid and 150 cc. of sulphuric acid (66° Bé.) in 850 g. of water. This process is slow and the treated surface has an irregular appearance. With alloys of copper, cobalt and beryllium, pickling is not complete.

In the other system, also a chromatosulphuric pickling process, the operation is carried out at a temperature within the range of 40–70° C. in a bath containing 50 g. chromic acid and 150 cc. sulphuric acid (66° Bé.) in 850 g. of water. Treatment is effected for one minute to produce a satisfactory surface even with copper-cobalt-beryllium alloys. Unfortunately, the process is troublesome because the bath deteriorates rapidly by reason of the reduction of the chromic acid in the bath.

It is an object of this invention to provide a method and means for removal of oxides from the surfaces of copper-beryllium alloys of the types described by a pickling process which is safe and efficient and which gives good results from the standpoint of appearance and surface finish, and in which the desired pickling process can be carried out without difficulty and in a short space of time.

In accordance with the practice of this invention, the usual chemical pickling process is replaced by an electrolytic pickling process in which use is made of an aqueous electrolyte solution containing at least one alkali metal halide and a surface active agent. The process of this invention is applied to the cleaning of copper-beryllium alloys having an oxide layer, such as the type produced during thermal treatment of the alloy, even when carried out in an inert atmosphere.

The following will list some of the principal advantages of the process of this invention. Pickling can be carried out rapidly, the treatment is applicable to ternary alloys containing up to 2.7% cobalt or nickel as well as to alloys containing 1.8–2% beryllium with a small amount of cobalt or nickel; it gives a fine and uniform metallic appearance to the pickled parts; and it is capable of continuous operation as well as batch operation and it makes use of an electrolyte formulated of readily available, low cost materials thereby to provide an inexpensive and economical pickling process.

In a preferred practice of this invention, the metal to be pickled is connected to the anode of a direct current generator while the cathode is an inert conductor, such as stainless steel. The electrolysis bath is formulated of a solution of sodium chloride in water with a surface active agent to assist in the removal of the greyish black oxide which forms as a deposit during pickling. The wetting agent releases the deposit for removal.

The concentration of materials making up the electrolyte and the operating conditions, such as current density, can be varied over fairly wide limits. For example, the concentration of sodium chloride or other alkali metal halide can be varied within the range of 100 and 200 g. per liter. The pH of the bath can vary within the range of 5.5 to 8.5 and the temperature of the bath can be varied within the range of 25–45° C. The voltage at the terminals is of the order of about 2 volts with a current density within the range of 3–5 amperes per square decimeter.

As the wetting or surface active agent, use can be made of an alcohol or a commercial wetting agent such as an anionic, cationic or nonionic surface active agent which is compatible with the pH of the bath and which are of the type described in "Oil and Soap," vol. XVII, No. 9, September 1941 (pages 179–182), by Harris, Epstein & Kohn. The amount of wetting agent depends upon its composition. If an alcohol is used, such as ethanol or methanol, the amount employed should be within the range of 50–100 g. per liter. In the event that use is made of a commercial surface active agent, the amount generally employed is within the range of 1–5 g. per liter.

The pickling treatment can be varied from 2–15 minutes depending somewhat on the thickness and character of the oxide layer on the metal surface. After pickling, the part is rinsed with water to remove electrolyte and then dried.

The following examples are given by way of illustration, but not by way of limitation, of the practice of this invention:

EXAMPLE 1

Strips of copper-beryllium alloy having 1.9% by weight of beryllium and 0.3% by weight of copper, tempered in an inert atmosphere had an oxidized surface following tempering treatment. The strips were pickled by electrolysis in an aqueous bath containing 200 g. per liter sodium chloride and 77 cc. per liter methanol.

The cathode was formed of stainless steel plate and the strip of metal was connected to the anode and passed through the electrolytic bath at a speed such that the residence time in the electrolyte was 3 minutes. The voltage at

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the terminals was 2 volts and the current density was 5 amperes per square decimeter.

Upon removal from the bath, the strip was rinsed in clean running water and dried, and the metallic appearance obtained was very uniform.

EXAMPLE 2

The elements, consisting of copper-cobalt-beryllium alloy, having 2.5% by weight cobalt and 0.5% by weight of beryllium, were oxidized during thermal treatment and suspended from the anode for immersion in a bath containing 150 g. per liter sodium chloride and 2 g. per liter Celanol A (a neutral polyethoxyether surface active agent).

Pickling was continued for 10 minutes at 35° C. with a terminal voltage of 2 volts and current density of 5 amperes per square decimeter. The elements were removed and rinsed in clean running water and dried. A complete and very regular pickling was obtained which gave a uniform appearance to the metal surface.

The metal halides and other surface active agents may be employed in the processes of Examples 1 and 2 without departing from the spirit of the invention, and other changes may be made in the details of formulation and operating conditions without departing from the spirit of the invention, especially as defined in the following claims.

I claim:

1. A process for pickling copper based alloys including at least 0.4% beryllium and up to 2.5% nickel or up to 2.7% cobalt, comprising the steps of connecting the alloy with the anode in a direct current electrolysis bath in which the bath consists essentially of an aqueous solution of an effective amount of a salt supplying chloride ions and a surface active agent, adjusting the pH of the bath to a value within the range of 5.5 to 8.5, and applying an electrical current between the anode and cathode at a cur-

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rent density which does not effect metal removal and while maintaining the bath at a temperature within the range of from about 20° C. to about 45° C.

2. The process as claimed in claim 1 in which the chloride salt is sodium chloride.

3. The process as claimed in claim 1 in which the chloride salt is present in the dissolved state in the bath in an amount within the range of 100-200 g. per liter.

4. The process as claimed in claim 1 in which the surface active agent is an alcohol present in an amount within the range of 50-100 g. per liter.

5. The process as claimed in claim 1 in which the surface active agent is selected from the group consisting of an anionic, cationic and nonionic surface active agent present in an amount within the range of 1-5 g. per liter.

6. The process as claimed in claim 1 in which the electrolytic bath has a pH within the range of 5.5-8.5 and is maintained at a temperature within the range of 20-45° C. during pickling.

7. The process as claimed in claim 1 in which the pickling is carried out by passing a current density of 3-5 amperes per square decimeter through the cell with the alloy connected to the anode.

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