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3,326,644

ELECTROWINNING COPPER AND PRODUCT THEREOF

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No Drawing. Filed Dec. 12, 1963, Ser. No. 335,707
4 Claims. (Cl. 29—180)

ABSTRACT OF THE DISCLOSURE

A process, and the product produced thereby, for electrolytically producing copper in the form of intermeshed filaments having a wool-like appearance utilizing a molten electrolyte at a temperature of 750° C. to 900° C. Direct current, at a cathode current density of 1,000 to 40,000 amperes per square foot is passed through the electrolyte which contains at least 25 grams per liter of dissolved monovalent copper and one or more fused alkali or alkaline earth metal halide salts and the copper is deposited at the cathode.

The present invention is directed to an improved process for the electrodeposition of copper and to novel electrodeposited copper obtained therefrom.

It is an object of this invention to provide an improved process for the electrodeposition of copper. It is also an object of this invention to provide a process for electrorefining copper. This invention also contemplates providing a process for electrowinning copper. It is still a further object of this invention to provide novel electrodeposited copper.

This invention contemplates electrodepositing copper from a fused salt electrolyte containing copper in the monovalent state. The copper electrodeposit which is formed at the cathode is in the form of intermeshed filaments which have a characteristic wool-like appearance.

The fused salt electrolytes useful in this invention are composed of at least one, and preferably a mixture of more than one, of the alkali metal halides and alkaline earth metal halides. The chlorides are preferred. These include sodium chloride, potassium chloride, lithium chloride, magnesium chloride, calcium chloride, strontium chloride, and barium chloride. Generally those electrolytes having lower melting points and lower viscosities are preferred. Illustrative of the preferred electrolytes are: Mixtures of potassium chloride and sodium chloride; a mixture of lithium chloride with sodium or potassium chloride; a mixture of calcium chloride with sodium or potassium chloride; and a mixture of barium chloride with calcium chloride. The eutectic mixtures are preferred because of the lower melting points. The preferred electrolyte may vary for different processes and different conditions. Electrolytes containing large proportions of calcium chloride are likely to introduce some oxygen into the bath and the resultant deposited copper. Such an electrolyte would not be preferred for electrodepositing high purity copper. It might be economical and suitable for an "upgrading" electrorefining operation wherein an impure copper (60–70% copper) is used as the anode to produce a higher copper cathode (e.g. 90–97% copper). The presence of small amounts of oxygen in such a product would not be significant.

The electrolysis is carried out in a cell formed from refractory materials (e.g. quartz, and the acid or basic refractories). The usual cell will have an anode and cathode separated by electrolyte, all in the same chamber. For special processes, divided cells wherein the anolyte and catholyte are separated may be utilized. The electrolytic cells known for the production of sponge metals,

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e.g. titanium sponge, from fused salt electrolytes may be used in this process. The usual electrorefining operation of this type is in the nature of a batch process in that the anodes and the cathodes are periodically pulled. Continuous processes may be utilized.

The electrolytic cell may be operated at standard atmospheric conditions. For specified purposes a closed system, and/or a vacuum or an inert atmosphere may be used.

The cathodes, which may be wire or rod, are preferably large flat bars so that high current throughput and high production are achieved. They may be formed from copper, stainless steel, chromium or chromium plated metals, titanium, platinum and other metals which are inert to the electrolyte and components thereof and have good conductivity. It is contemplated that soluble copper-containing anodes will be used in most of our processes. The copper is anodically dissolved during the electrolysis. It is also contemplated that copper may be added to the bath in the form of copper salts, e.g. CuCl or CuCl₂ which rapidly converts to Cu⁺, to supply the necessary copper concentration of the bath or to supplement the copper which is anodically dissolved into the bath. Graphite anodes would be preferred if copper chloride were the source of copper in the bath. With correct design of the size and spacing of the anodes and cathodes, it is possible to regulate the bath so that additions of copper in the form of copper salts need not be made directly to the bath. Where it is desired to raise the copper content of the bath, chlorine may be introduced into the electrolyte in the vicinity of the anode while the bath is molten to react with the copper anode and to dissolve copper into the electrolyte. This expedient is also useful in preparing the electrolyte for electrolysis of copper.

Copper is dissolved in the electrolyte to enable electrodeposition of copper under the conditions contemplated. When the concentration of copper drops below about 25 g./l., the back E.M.F. increases resulting in lowered cathode efficiency, particularly at high current densities.

It is contemplated that copper may be electrodeposited at current densities between about 50 amperes per square foot (a.s.f.) up to as high as about 40,000 a.s.f. With the usual cell wherein the spacing between the anodes and cathodes is about four inches, it is not contemplated that the current density will be more than about 5,000 to 6,000 a.s.f. Where higher current densities are used, the heat generated at the anode and cathode may cause fusion. For economical commercial operation wherein high current densities result in high throughput with given equipment, it is preferred that the current densities be between 1,000 a.s.f. and 5,000 a.s.f. The voltage will vary with cell design, particularly anode and cathode spacing, and bath temperature.

The electrolysis may be carried out at all temperatures at which the electrolyte is molten. It is generally preferred that the temperature should not be higher than about 900° C. to prevent vapor losses when low melting salts, e.g., the eutectic mixture of sodium and potassium chloride with a melting point of about 650° C., are used in an open cell.

It has been discovered that electrodeposition carried out just above the melting point of the electrolyte is less efficient than that carried out at higher temperatures. The voltage drop across the cell is relatively high just above the melting point of the electrolyte and becomes less as the temperature is raised. This is illustrated in the behavior of the cell prepared from the preferred eutectic potassium chloride-sodium chloride mixture. The voltage drop at 750° C. in the cell tested was 680 millivolts. At 800° C., the voltage drop was only 390 millivolts, and at

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850° C., 380 millivolts. The temperature at which the voltage drop is significantly lowered varies somewhat for different electrolytes. Electrodeposition between about 800° C. and 900° C. is generally preferred.

The copper is electrodeposited at the cathode in the form of filaments which are intermeshed and have a wool-like appearance. The copper filaments are easily scraped off the cathode with very light pressure. After water leaching to remove bath salts and adherent impurities, the deposits may be hydrogen annealed and rolled into sheets of copper. It has been found that the electrorefining operation operates to lower the sulfur and oxygen content when high purity copper is utilized as the soluble anode.

After a sufficiently long electrolysis, purification of the electrolyte may be required. This may be carried out in a batch process or may be carried out continuously by bleeding off and refining a portion of the electrolyte.

The invention is further illustrated in the examples but is not to be construed as limited to details described therein. The parts and percentages are by weight except where specifically indicated otherwise.

The electrolyses were conducted in a quartz crucible measuring 9¼ inches deep and 8 inches in diameter. The crucible was heated to the specified temperature with a resistance wound furnace. The direct current power supply originated from two sources, (1) a 100 ampere ten volt rectifier maximum stepwise control used in Examples 1-4, and (2) a 2000 ampere 6 volt rectifier maximum with stepwise control used in Example 5. All of the electrolyses were carried out using as the electrolyte, the eutectic mixture of potassium chloride and sodium chloride (1.3 KCl to 1 NaCl by weight).

Example 1

A series of tests were carried out utilizing sheet anodes and cathodes, four inches by four inches spaced about one inch apart. The copper concentration in the electrolyte was approximately 20 g./l. Electrolysis was carried out at 750° C., 800° C. and 850° C. The voltage drop at 750° C. (using 100 amperes) was 680 millivolts. At 800° C., the voltage drop was 390 millivolts and at 850° C. the voltage drop was 380 millivolts. In all cases the copper produced at the cathode was in the form of intermeshed threads having a wool-like appearance.

Example 2

Highly pure copper sheets were used as the anodes. Drawn copper wires (0.08 inch and 0.12 inch) were used as cathodes to obtain a high current density. By regulation of current and submersion of cathode, the initial current density was varied from 50 a.s.f. to 40,000 a.s.f. The bath contained between 20 and 30 g./l. of copper. The distance between the anodes in different experiments was 1 or 2 inches. Highly pure oxygen-free copper anodes were utilized. A number of runs were conducted and it was determined that the current efficiency (based on monovalent copper deposition) varied from 31% to 100%. It was established that the low current efficiency runs were due to shorts between anodes and cathodes. All the deposits of copper were composed of intermeshed filaments and had the characteristic wool-like appearance. After water leaching, most of the deposited material was still sticking together in the form of an irregular balled mass of intermeshed filaments. These deposits after leaching and hydrogen annealing could be rolled into sheets. The deposited copper was very pure.

Example 3

Similar conditions to Example 2 were utilized except that the spacing between anodes and cathodes was increased to four inches to prevent shorting. The current density was varied from 500 to 40,000 a.s.f. The temperature was held to about 800° C. (plus or minus 25° C.). The concentration of copper in the electrolyte varied

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from 18 to 35 g./l. The anodes were prepared from "tank house anode copper" which is a relatively pure copper. It was determined that at 18 g./l. of copper in the electrolyte abnormally high voltages and back e.m.f. were obtained which resulted in low cathode current efficiency, particularly with cathode current densities of 1000 a.s.f. or higher. When the copper concentration of the electrolyte was increased to 25 g./l., the voltage drop across the anode and cathode returned to normal. In all cases the copper electrodeposits had the characteristic wool-like appearance. They were highly pure. The process appears to diminish, or eliminate, sulfur and oxygen.

Example 4

The same equipment and procedure described in the preceding examples was utilized. Deposits were obtained over a range of current densities. The temperature was held at about 800° C. The cathode current efficiency was about 100%. The anode current efficiencies varied from about 87% to about 90% in different runs. The anodes utilized were prepared from "black copper," an impure copper having a copper content of between 60 and 70%. The results for the electrolysis indicated under this example are the same as those noted and described in Example 5.

Example 5

The same impure copper utilized as the anode in Example 4 was also utilized in these runs. The same equipment was utilized except that the cathode was changed from wire to bus-bar copper 1½ inches by 4 inches, having a thickness of ¼ inch (4 inches submersion) resulting in a total cathode surface of ¼₁₀ sq. ft. The anode was the impure copper, 4 inches by 20 inches by ⅞ inch (4 inches submersion). The product for each of a series of runs had the characteristic wool-like appearance. The copper content in the product from different runs varied from 90-97%. The iron content of the electrodeposited copper varied from about 1 to about 5%. The nickel content of the impure anode was about 4%. The corresponding nickel content of the electrodeposited copper varied from 1 to 3%. The arsenic, antimony, lead and tin contents of the electrodeposited copper were substantially less than that of the impure anode. The results of Examples 4 and 5 illustrate the use of the process as a method of substantially upgrading impure copper.

From the results of the experiments it was determined that copper was deposited from the monovalent state. The process may be operated at above 8.5% cathode current efficiency. Under controlled conditions operation at a cathode current efficiency between 95% and 100% can be achieved.

In all the experiments, it was observed that the soluble copper-containing anodes dissolved uniformly. In addition to the electrolysis utilizing soluble anodes illustrated in the examples, it was found that similar results can be obtained from electrolytes made up with dissolved copper. Such runs were of short duration due to the depletion of copper and the dropping of the copper concentration below the desired level. This would be avoided if soluble copper salts were continuously introduced into the electrolyte. Experiments were also carried out with melts prepared from calcium chloride, barium chloride, strontium chloride, potassium chloride, and sodium chloride, and it was determined that these melts had characteristics similar to those for the eutectic potassium chloride-sodium chloride mixture described in detail with reference to the particular examples.

Obviously, many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A process for the electrolytic deposition of copper in the form of intermeshed filaments having a wool-like

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appearance which comprises providing a molten electrolyte having a temperature of between 750° and 900° C. and containing at least 25 grams per liter of dissolved copper therein in the monovalent state as well as a fused salt selected from the group consisting of alkali metal halides, alkaline earth metal halides and combinations thereof, passing direct current through a cell having an anode, a cathode and said molten electrolyte at a cathode current density of between 500 and 40,000 amperes per square foot and depositing intermeshed filaments of copper at the cathode.

2. The process of claim 1 wherein the temperature of the molten electrolyte is between 800° and 900° C. the fused salt is the eutectic mixture of potassium chloride and sodium chloride and the cathode current density is between 1,000 and 5,000 amperes per square foot.

3. The process of claim 1 wherein at least a portion of the copper in the molten electrolyte is provided by a copper-containing anode.

4. The copper product produced by the electrolytic

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process of claim 1; said product being in the form of intermeshed filaments having a wool-like appearance.

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