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The file contains technical information submitted after the application was filed and not included in this specification

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Description

This invention relates to an electrodeposition cell having a rotating cylindrical deposition electrode and to a method of removing deposit from such an electrode.

Rotating cylindrical cathodes for recovering metals from dilute salt solutions in electrodeposition cells are known, for example from GB Patent Specification No. 1505736. Depending on the current density, the peripheral speed of the rotating cylinder, and the salt concentration, the metal may deposit as a loosely adherent deposit which is washed off the cathode. However, the current that can be passed through a freshly washed cathode is much less (e.g. six to sixty times less) than can be passed through a cathode bearing a rough deposit, at comparable current efficiencies. For this reason GB—A—1505736 advocates pre-roughening the cathode. GB—A—1505736 also suggests that a reciprocating scraper extending over part only of the length of the cathode may be provided, but states no special technical advantage.

US—A—3619389 discloses a static cathode which however is continuously roughened by an abrasive continuous activating belt, which also maintains, by entrainment, a high rate of supply of electrolyte to the cathode and removes the electrodeposit. This arrangement is cumbersome and complicated, and would require very careful control of the exact positions of the anode and cathode on opposite sides of the belt.

US—A—1535577 discloses apparatus for the electrolytic deposition of metals, comprising a rotating cathode and a scraper operating on the cathode to remove metal which has been electrodeposited on it. The scraper is fixed in operation but is ajustable radially of the cathode to regulate the thickness of the metal allowed to grow on the cathode. The scraper is the same height as the cylindrical cathode and therefore operates on the whole cylindrical area every revolution.

The invention is an electrodeposition cell having a rotating cylindrical deposition electrode and a scraper engaging the electrodeposit and breaking away its outer portion for removing deposit from that electrode, such that, in operation, the electrode retains a substantially rough electrodeposit, characterised in that the axial extent of the engaging part of the scraper does not exceed half the axial extent of the electrode, the engaging part being axially movable so that, with the electrode rotating, the scraper can engage any point on the electrodeposit.

The engaging part may be arranged to be axially movable by making the scraper axially movable, or the scraper may comprise a rotatable helical blade whose axis is parallel to the cylinder axis; rotation of the scraper about its own axis will thus cause the contact area to traverse the electrode axially.

The axial extent of the part of the scraper at any instant engaging the electrode preferably does not exceed 0.1 of the axial extent of the electrode, more preferably does not exceed 0.01 thereof, most preferably does not exceed 0.002.

The invention is also a method of removing deposit from a rotating cylindrical deposition electrode in an electrodeposition cell during electrodeposition, such that the electrode retains a substantially rough electrodeposit, comprising applying to the electrodeposit, such that it will not bare the electrode, a scraper breaking away the outer portion of the electrodeposit, characterised in that the scraper scrapes not more than 0.1 of the cylindrical area of the electrode in one revolution thereof. In this way, the electrodeposit stays at least microscopically rough even the instant after some has been removed. Preferably the scraper scrapes not more than 0.01, most preferably not more than 0.002 of the cylindrical area of the electrode in one revolution thereof.

The scraper may comprise a helical blade (as described above) or may comprise a full-axial-extent blade brought into contact with the electrode for only a fraction of a revolution or may comprise a part-axial-extent blade mounted on an axially-moving carrier so that, as the electrode rotates, the scraping follows a helical path (like a screw thread) over the area of the electrode. The carrier may spring back to its starting point after the whole electrode is scraped or may move backwards at the same rate as forwards. The scraper may contact the electrodeposit continuously, or may contact it intermittently. The degree of contact is such as to scrape off the outer portion only of the deposit.

In this way, a continuous stream of deposit can be removed from the electrode and collected from the bottom of the cell, while the electrode remains rough over its area and hence retains a much higher current capacity than if the electrode had been washed or a doctor blade wiped the whole cylindrical surface to bareness every revolution. The roughness is superior to roughening expedients such as knurling the electrode. Indeed, thanks to the permanent high average roughness, mixing in the region immediately around the cylinder approaches theoretically perfect mixing, and therefore the flow-rate through the electrodeposition cell does not affect mass transfer rates to the electrode. Such high yet constant mass transfer is an unusual achievement in chemical reactions. Also, the contact area between the scraper and the electrode is a negligible fraction of the cylindrical area, and hence the scraper physically obstructs electrodeposition but negligibly. The roughness affords a high true surface area on a relatively small-volume electrode.

The invention will now be described by way of example with reference to the accompanying drawings, in which:—

Figure 1 shows a deposition electrode and scraper from a cell according to the invention, and

Figure 2 shows an electrode and alternative scraper from a cell according to the invention.

In Figure 1, a cathode 1 of an electrodeposition cell (which, being otherwise standard, is not further shown or described) is of cylindrical form, diameter 60 mm and height 63 mm, and is driven at 360 revolutions per minute (peripheral velocity: 1.13 m/s) by a motor 2. An upright carrier 4, reciprocated by a pneumatic actuator 5, carries a scraper point 4a contacting the cathode 1 at an area whose height (parallel to the cylinder axis) is 1 mm. It is enlarged on the drawing for clarity.

The cathode 1 is in an aqueous electrolyte of 1.5 M sulphuric acid H_2SO_4 plus 0.014 M copper sulphate $CuSO_4$ ât 22°C. The Reynolds number at its surface is about 59000.

In use of a brand new hydrodynamically smooth cathode 1, a stop (not shown) holds the scraper point 4a clear of the cathode 1 and a voltage of approximately 2.5 V is applied. Current starts to flow at 0.8 A, in good accordance with theory, and after about 20 minutes the copper depositing on the cathode begins perceptibly to roughen it. The current starts to rise, after 1 hour reaching 3 A (the maximum possible at that current efficiency with a knurled cylinder having a peak-to-valley roughness of 1 mm, according to Kappesser et al, J. Electrochem Soc *118* (1971) p. 1957). Contrary to the Kappesser teaching, however, the current continues to rise, tending to level off at about 6A after 2½—3 hours.

The stop is withdrawn, and the scraper point 4a contacts the electrodeposit on the cathode 1. This electrodeposit is rough. Copper powder is scraped off by a dendrite-fracturing action and is collected, as schematically indicated at 6. The actuator 5 pulls the carrier 4 downwards slowly at such a rate (3 mm/minute) that the point 4a leaves a helical trail on the cathode 1, the trail taking about 20 minutes to cover every part of the cylindrical area of the cathode 1. The trail having been formed by a fracturing action, it is rough even when newly formed, and can maintain a current density substantially higher than that predicted by Kappesser, recovering to its maximum after about 1 minute.

Immediately the point 4a has scraped an element of the cathode 1, electrodeposition resumes and the trail eventually disappears (as shown oversimplified in Figure 1), and there are 20 minutes' worth of electrodeposition to be scraped off when the point (or rather the leading edge of the point) 4a returns to that element. The carrier 4 preferably flies back to its starting point or may move upwards and downwards (20 minutes each) at the same speed. Even while scraping is proceeding, the current is maintained at substantially 5.7 A; a smooth cathode could pass only 0.8 A at that voltage.

Turning to Figure 2, a cathode is shown identical to that in Figure 1, but the scraper differs. The scraper 14 is in the form of a helical blade making just one rotation in the height of the cathode and driven by a slow-speed motor 15 at one revolution per 20 minutes.

A part-height or helical scraper fractures off the dendritic electrolytic deposits, leaving a beneficial underlying microroughness; a full-length scraper might bare the cathode and even burnish it, whereby the current density would regress to that described in relation to a brand new cathode. This fracturing action also has the advantage of yielding a powder product reasonably consistent in size and type.

If the frequency with which the scraper traverses any given point on the cathode is too low, and trials will readily establish this, the electrodeposit becomes excessively rough and the energy required to rotate the rough cathode becomes correspondingly excessive. For some metals and electrolytes, this excessive roughness takes the form of spindly dendrites which can drop off randomly and which are of inconsistent quality. they can drop off in such a way as to lead to a 'peeling' of the electrodeposit; in catastrophic cases, up to 10% of the burden can be shed in this way, unbalancing the cathode to the detriment of its driving mechanism. The spindly dendrites may also damage any nearby diaphragm or membrane.

Claims

1. An electrodeposition cell having a rotating cylindrical deposition electrode and a scraper engaging the electrodeposit and breaking away its outer portion for removing deposit from that electrode, such that, in operation, the electrode retains a substantially rough electrodeposit, characterised in that the axial extent of the engaging part (4a, 14) of the scraper does not exceed half the axial extent of the electrode (1), the engaging part being axially movable so that, with the electrode rotating, the scraper can engage any point on the electrodeposit.

2. A cell according to Claim 1, characterised in that the axial extent of the engaging part (4a, 14) of the scraper does not exceed 0.1 of the axial extent of the electrode (1).

3. A cell according to Claim 1, characterised in that the axial extent of the engaging part (4a, 14) of the scraper does not exceed 0.01 of the axial extent of the electrode (1).

4. A cell according to Claim 1, characterised in that the axial extent of the engaging part (4a, 14) of the scraper does not exceed 0.002 of the axial extent of the electrode (1).

5. A cell according to any preceding Claim, characterised in that scraper (4) is axially movable.

6. A cell according to any preceding Claim, characterised in that the scraper comprises a rotatable helical blade (14) whose axis is parallel to the cylinder axis.

7. A method of removing deposit from a rotating cylindrical deposition electrode in an electrodeposition cell during electrodeposition, such that the electrode retains a substantially rough electrodeposit, comprising applying to the electrodeposit, such that it will not bare the electrode, a scraper breaking away the outer portion of the electrodeposit, characterised in that the scraper scrapes not more than 0.1 of the cylin-

drical area of the electrode in one revolution thereof.

Revendications

1. Cellule d'électrodéposition, comportant une électrode rotative cylindrique de déposition et un racleur venant au contact du dépôt électrolytique et en enlevant par rupture la partie externe pour enlever le dépôt de cette électrode de façon que, en service, l'électrode conserve un dépôt électrolytique essentiellement rugueux, cellule caractérisée en ce que l'étendue axiale de la patie en contact (4a, 14) du racleur n'excède pas la moitié de l'étendue axiale de l'électrode (1), la partie venant en contact étant axialement mobile de sorte que, avec l'électrode en rotation, le racleur peut venir au contact de n'importe quel point du dépôt électrolytique.

2. Cellule selon la revendication 1, caractérisée en ce que l'étendue axiale de la partie (4a, 14) du racleur venant en contact avec le dépôt n'excède pas 0,1 fois l'étendue axiale de l'électrode (1).

3. Cellule selon la revendication 1, caractérisée en ce que l'étendue axiale de la partie (4a, 14) du racleur venant au contact du dépôt n'excède pas 0,01 fois l'étendue axiale de l'électrode (1).

4. Cellule selon la revendication 1, caractérisée en ce que l'étendue axiale de la partie (4a, 14) du racleur venant au contact du dépôt n'excède pas 0,002 fois l'étendue axiale de l'électrode (1).

5. Cellule selon n'importe quelle revendication précédente, caractérisée en ce que le racleur (4) est mobile axialement.

6. Cellule selon l'une quelconque des revendications précédentes, caractérisée en ce que le racleur comprend une lame (14) hélicoïdale rotative dont l'axe est parallèle à l'axe du cylindre.

7. Procédé pour enlever un dépôt d'une électrode cylindrique rotative de dépôt dans une cellule d'électrodéposition pendant l'électrodéposition, de sorte que l'électrode conserve un dépôt électrolytique essentiellement rugueux, comprenant l'application, au dépôt électrolytique, de façon à ne pas dénuder l'électrode, d'un racleur qui enlève par rupture la partie externe du dépôt électrolytique, procédé caractérisé en ce que le racleur ne racle pas plus de 0,1 fois la surface cylindrique de l'électrode en un tour de celle-ci.

Patentansprüche

1. Zelle zur elektrolytischen Abscheidung mit drehbarer zylindrischer Abscheidungs-Elektrode und einem Schaber, der das abgeschiedene Material angreift und aufbricht an seinem Austrennteil zu dessen Abnahme von der Elektrode, so daß diese während des Betriebs einen im wesentlichen rauhen Abscheidungs-Überzug beibehält, dadurch gekennzeichnet, daß das axiale Ausmaß des einwirkenden Teils (4a, 14) des Schabers sich nicht über mehr als die Hälfte der axialen Stärke der Elektrode (1) erstreckt und dieser eingreifende Teil axial derart bewegbar ist, daß der Schaber bei der Umdrehung der Elektrode auf jeden Punkt der Abscheidungsschicht einzugreifen vermag.

2. Zelle nach Anspruch 1, dadurch gekennzeichnet, daß sich der einwirkende Teil (4a, 14) des Schabers axial um nicht mehr als 0,1 der axialen Dicke der Elektrode (1) erstreckt.

3. Zelle nach Anspruch 1, dadurch gekennzeichnet, daß sich der einwirkende Teil (4a, 14) des Schabers axial um nicht mehr als 0,01 der axialen Dicke der Elektrode (1) erstreckt.

4. Zelle nach Anspruch 1, dadurch gekennzeichnet, daß sich der einwirkende Teil (4a, 14) des Schabers axial um nicht mehr als 0,002 der axialen Dicke der Elektrode (1) erstreckt.

5. Zelle nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Schaber (4) axial bewegbar ist.

6. Zelle nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Schaber ein drehbares schneckenförmiges Band (14) umfaßt, dessen Achse parallel zur Zylinderachse liegt.

7. Verfahren zur Entfernung von Abscheidungs-Material von einer zylindrischen drehbaren Elektrode für die Elektroabscheidung während des Betriebs, wobei auf der Elektrode eine im wesentlichen rauhe Abscheidungsschicht verbleibt, mit Hilfe eines die Elektrode nicht freilegenden Schabers, der die äußeren Teile der Abscheidungsschicht wegzubrechen vermag, dadurch gekennzeichnet, daß der Schaber nicht mehr als 0,1 der Zylinderfläche der Elektrode bei einer Umdrehung überstreicht.

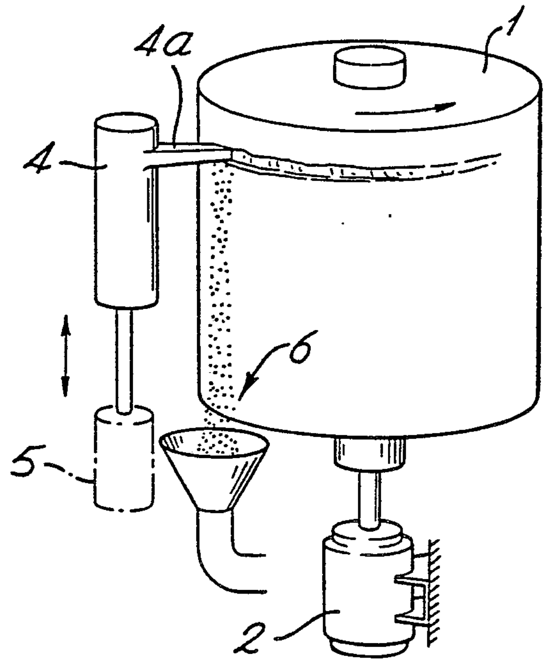

Fig. 1

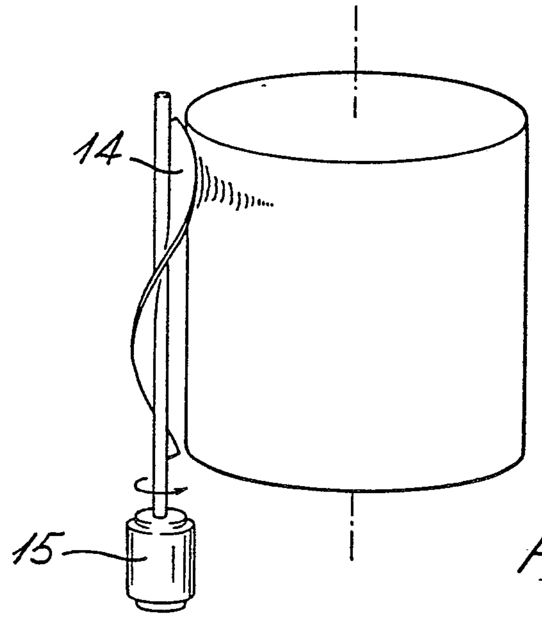

Fig. 2