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ELECTROLYTIC FUSION CELLS AND METHOD OF OPERATING THE SAME

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Fig. 1

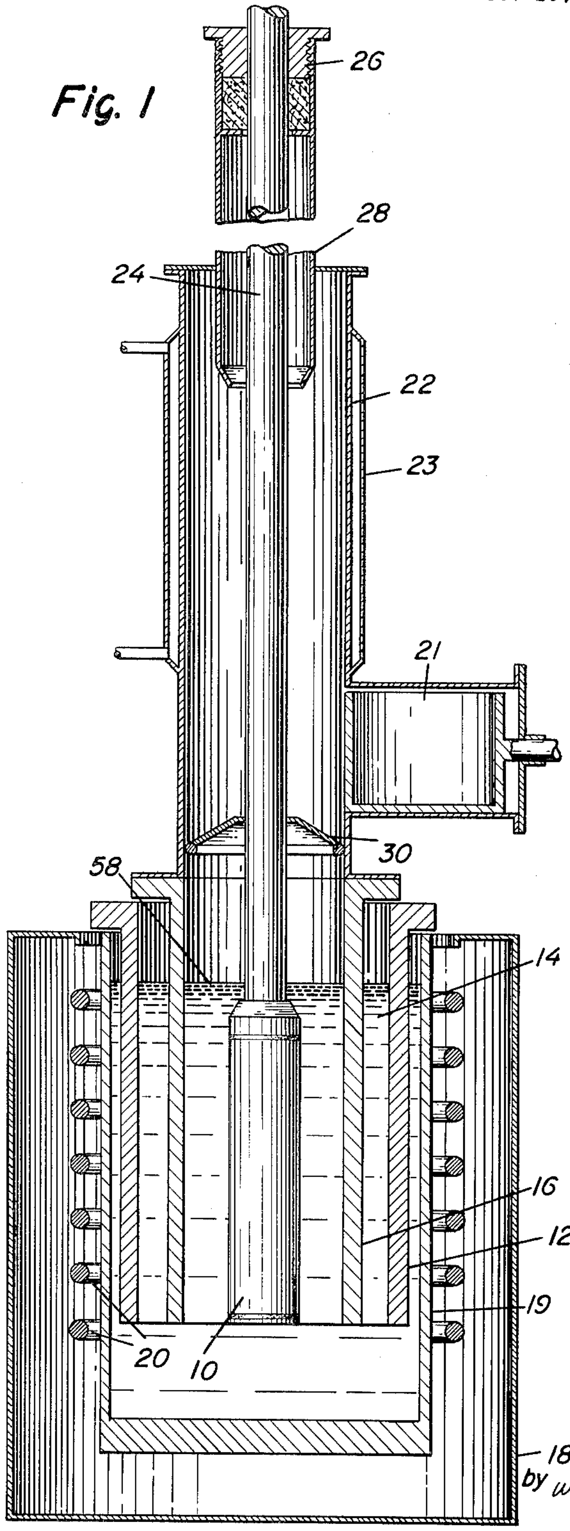
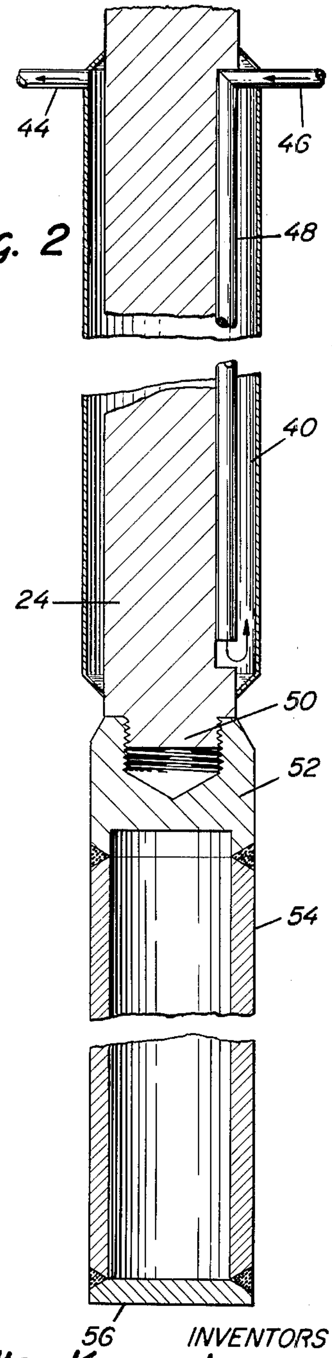


Fig. 2



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ELECTROLYTIC FUSION CELLS AND METHOD OF OPERATING THE SAME

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5 Claims. (Cl. 204—64)

The present invention relates to cells for fusion electrolysis having a cathode arranged centrally within an anode.

When carrying out fusion electrolysis for obtaining metals, cells are usually employed in which the cathode, which serves for metal deposition, is as a rule rod-shaped and is located centrally within an annular anode. The temperature of the melt in which the cathode is submerged is generally within the range of about 400 to 900° C. Thus, the cathode is subjected to strong corrosion due partly to the comparatively high temperature of the melt and partly to the composition of the latter. It has already been proposed to cool the cathode in cells of the construction just described.

According to the present invention, a cell for fusion electrolysis comprises a cathode arranged centrally within an anode, the cathode being supported by a cathode-supporting device which serves also as a current supply lead for the cathode and has a cooling system.

An embodiment of the present invention will now be described in further detail with reference to the accompanying drawings of which

FIG. 1 is a diagrammatic section of the basic construction of the embodiment, and

FIG. 2 is a sectional view of the cooling arrangement of the cathode-supporting device.

FIG. 1 shows the basic construction of the cell which consists of the rod-shaped cathode **10** arranged centrally within an anode **12** of annular or sleeve-like form. The cathode is made from a highly corrosion-resistant metal, for example nickel. The annular anode **12** is made of graphite. The anode is contained in a crucible **19**, for example of graphite, containing a melt **14**. Generally, alkali metal chloride melts, such as sodium chloride or potassium chloride or the eutectic mixtures of such chlorides are used in which the metal is dissolved in the form of the chloride, fluoride or fluoride double salt. A cylindrical diaphragm **16** is located between the cathode **10** and the anode **12** to separate the cathode space from the anode space, in order to protect the separated metal from the halide liberated on the anode wall. The anode **12** and the crucible **19** are contained in a housing **18** which, at the same time, serves as a thermal insulation, electric heating coils **20** being located between the housing **18** and the crucible **19** for heating the melt.

Above the cell is located a protective housing **22** arranged to prevent oxygenous atmosphere entering the cell so that the separated metal cannot absorb oxygen from the atmosphere when being removed from the cell. Usually an inert atmosphere, for example argon or helium, is maintained within the protective housing **22**. The cathode **10** is supported at its upper end by a supporting device **24** which serves not only as a mechanical supporting means but also as a current supply lead. During the process of electrolysis the supporting device **24** submerges slightly below the melt level **58**. The supporting device **24** passes through a gland **26** in the upper part of the protective housing **22**.

When sufficient metal has been deposited on the cathode **10** the cathode is removed upwardly by the supporting device **24** and the deposited metal removed from the

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cathode. To do this, a sleeve-like stripping device **28** is employed with a receptacle **21** to prevent metal stripped off by the sleeve **28** when the cathode is withdrawn upwardly falling back again into the melt. Arrangements of that form are described, for example, in U.S. patent application Ser. No. 122,524, filed July 7, 1961, now Patent No. 3,156,638.

The cathode-supporting device which serves also as a current supply lead for the cathode has a cooling system. Cooling may be effected by any desired fluid coolant, for example by a liquid coolant such as water, oil, etc. or by a gaseous coolant.

FIG. 2 shows in diagrammatic form part of the embodiment of FIG. 1 and shows a cathode-supporting device with cooling. The support rod **24** has a cooling sleeve **40** which extends over the entire length of the rod and which is spaced uniformly from the rod, thus creating a cooling space having the shape of a cylindrical cavity. Coolant is introduced into this cooling space through a feedpipe **46** and removed at the upper portion of the sleeve **40** through a discharge pipe **44**. A pipe **48** is set into the rod **24** to facilitate entry of the coolant into the sleeve **40** at the lowest point of the latter.

Obviously, the embodiment just described is only one of many alternative ways of cooling the support. It is also possible, for example, to employ instead simply a rod **24** having a large central bore through which the coolant is conducted. A preferred flow direction can be imparted to the coolant by the inclusion, for example, of baffle plates in the bore. In the embodiment shown, the cathode itself is secured to the lower end of the support rod by means of a threaded boss **50** on the device **24**.

A particularly advantageous subsidiary feature of the invention is the use of a cathode in the form of a hollow body. That cathode has an upper short solid portion **52** with a threaded bore which enables connection to the supporting device to be made. The hollow portion of the cathode which consists of a hollow cylinder **54** is fastened to the supporting device. The hollow cylinder is closed at the bottom end by means of a closure **56**.

The degree of cooling is such that the temperature of the cathode is higher and the temperature of the supporting rod lower than the freezing temperature of the melt. During a single deep immersion of the cathode in the melt and subsequent withdrawal to working level a layer of solidified melt forms on the cooled support rod. The cathode temperature is determined by the coolant temperature in the supporting device and is affected by the type of connection between cathode and the lower end of the supporting device which controls heat transfer from the cathode to the supporting device. At the same time, the temperature of the supporting device can be kept at a level which is above the dew point of the vapours produced above the melt. By thus arranging the temperatures maintained in the individual parts of supporting device and cathode, the best-possible protection of supporting device and cathode against corrosion is achieved. By always keeping the temperature of the support rod below the freezing temperature of the melt, the support rod is coated with a salt layer which severely reduces if not prevents access of corrosive substances; it must be remembered, however, that the freezing melt is, of course, not free from pores.

On the other hand, the temperature of the support rod is decreased to such an extent that the corrosive action of any substances which may still reach the metal surface is very considerably reduced. That makes superfluous the employment of a graphite sleeve for the protection of the support rod which, in such cells, would otherwise have to be employed. The employment of such a graphite sleeve does not of course afford absolute protection, since the corrosive substances can still diffuse through the graphite sleeve and penetrate into the narrow gap between sleeve and support rod. Once having penetrated, these substances exert a very strong corrosive action upon the support rod at this point.

Holding the temperature of the support rod at a value above the dew point of the vapours produced in the atmosphere above the melt prevents condensation of such vapours on the surface of the support rod. In any case, it is necessary to keep the temperature of the support rod above 100° C. so that under no circumstances is water allowed to condense upon this rod. The existence of condensed water leads to a large increase in corrosion of the holding rod because halides contained in the atmosphere, and particularly chlorine, form acids, for example hydrochloric acid, with any condensed water on the support rod, and the acids have a considerably stronger action than the corresponding dry halide.

Heat flow from the cathode to the support rod is minimized by suitable design of the connection between those parts. For example, in the embodiment described above, the cathode is fastened to the holding rod by means of a thread which is designed in such a way that the contact surface which determines the heat flow is considerably smaller than the cross section of the support rod. The thread has the further advantage that the cathode can easily be separated from the support rod. Other constructions may be used, for example a reduction of the cross section of the lower end of the holding rod by turning or drilling reduces heat transfer.

In a cell embodying the present invention, a cooling effect is produced especially on the support rod where it is desired. The cathode itself is only slightly cooled, on the other hand. The temperature difference produced at the junction between cathode and support rod enables the cooling effect to be adjusted in such a way that the temperature of the support rod can safely be kept below, and that of the cathode safely above the freezing temperature of the melt. At the same time, reduction of heat transfer ensures that a comparatively low heat loss occurs in a direction outwardly of the melt. Thus, the thermal energy required to maintain the melt temperature is kept at a minimum. Considerable advantages are also secured by the employment of a hollow cathode. The hollow cathode has a lower thermal capacity which means that when the cathode penetrates the melt, only a comparatively small amount of thermal energy is removed from the melt, in order to raise the cathode to the melt temperature. Therefore, when the cathode is periodically removed in order to remove deposited metal, and subsequently introduced again, a comparatively small amount of heat is removed from the melt. Furthermore, there is the advantage that once the cathode has been withdrawn from the melt in order to remove the metal, the cathode cools very quickly because the amount of heat contained in the cathode is small. Cooling by the cooling sleeve of the protective housing **23** is therefore sufficient to cool the cathode very quickly, and this again is very desirable for the removal of the metal from the cathode so as to prevent the separated metal from absorbing gas. As is known, when the cathode is withdrawn from the melt, the cathodic protection of cathode against corrosion by melt substances does no longer exist at first. However, after the removal cooling sets in very quickly so that any substances still present solidfy and then in practice exert no further corrosive action.

If necessary, the cooling effect can be varied in intensity during the different periods of the working cycle such that, for example, during the separation, cooling is provided to the extent required for maintaining the above-mentioned temperatures of cathode and cathode support. When the cathode has been removed from the melt, however, cooling is intensified so that quicker cooling of the withdrawn cathode and the removed metal takes place.

A further advantage of the arrangement described above, apart from the considerably reduced risk of corrosion of the cathode, is a quickened working cycle, due to the fact that the amount of heat contained in the hollow cathode is comparatively small. That results in a shortened cooling time. Further, due to the reduced risk of corrosion, the cathode can be re-employed without difficulty when the metal has been removed. This has not been possible hitherto because usually the cathode had to be cleaned after every separation cycle, in order to prevent progressive corrosion. The present arrangement therefore provides, first of all, a considerably more favorable exploitation of performance and energy, due to the reduced heat losses, and also an improved cell performance in time, because of the shorter stopping periods required during removal and re-introduction of the cathode. All this is achieved although only a single cathode is employed.

What is claimed is:

1. A cell for fusion electrolysis comprising an annular anode, a cathode centrally positioned within said anode, and a cathode-supporting device, said supporting device being mounted for vertical movement and extending vertically from said cathode, housing means surrounding said supporting device, said housing means being capable of receiving the cathode when the supporting device is upwardly withdrawn, said supporting device serving as a current supply lead to said cathode and having incorporated therein a cooling system employing a circulating fluid coolant, said cathode having the form of a hollow cylindrical element and being releasably joined to the said cathode-supporting device by a joint having such a configuration as to reduce heat transfer from the cathode to the supporting device.

2. A method for operating a fusion electrolysis cell as in claim **1** for the fusion electrolysis of a melt which comprises maintaining the temperature of the cathode above the freezing temperature point of the melt and the temperature of the cathode-supporting device below the freezing temperature of the melt and above the dew point of the vapors above the melt.

3. A cell for fusion electrolysis as defined in claim **1** wherein the cathode-supporting device is releasably connected to the cathode by screw-joint means and has circumferential cooling channels for maintaining temperature of said device at a predetermined level.

4. Cell of claim **3** wherein the screw-joint means comprises a threaded screw member of diameter substantially less than the diameter of the supporting device and the cathode, said screw member being integral with said supporting device and releasably joined to said cathode, whereby said cathode is supported and whereby heat transfer between said supporting device and said cathode is minimal.

5. A method of operating the cell of claim **3** for the fusion electrolysis of a melt comprising maintaining the cathode temperature above the freezing point of the melt, while maintaining the supporting device temperature below the freezing point of the melt but above the dew point of the vapors of the melt.

References Cited by the Examiner

UNITED STATES PATENTS

2,000,815	5/1935	Berl	204—262
2,739,115	3/1956	Call et al.	204—243
2,838,454	6/1958	Washburn	204—246
2,887,443	5/1959	Blue et al.	204—246
2,904,491	9/1959	Moles et al.	204—246
2,958,640	11/1960	Cichelli	204—246
2,987,462	6/1961	Chauvin et al.	204—245

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