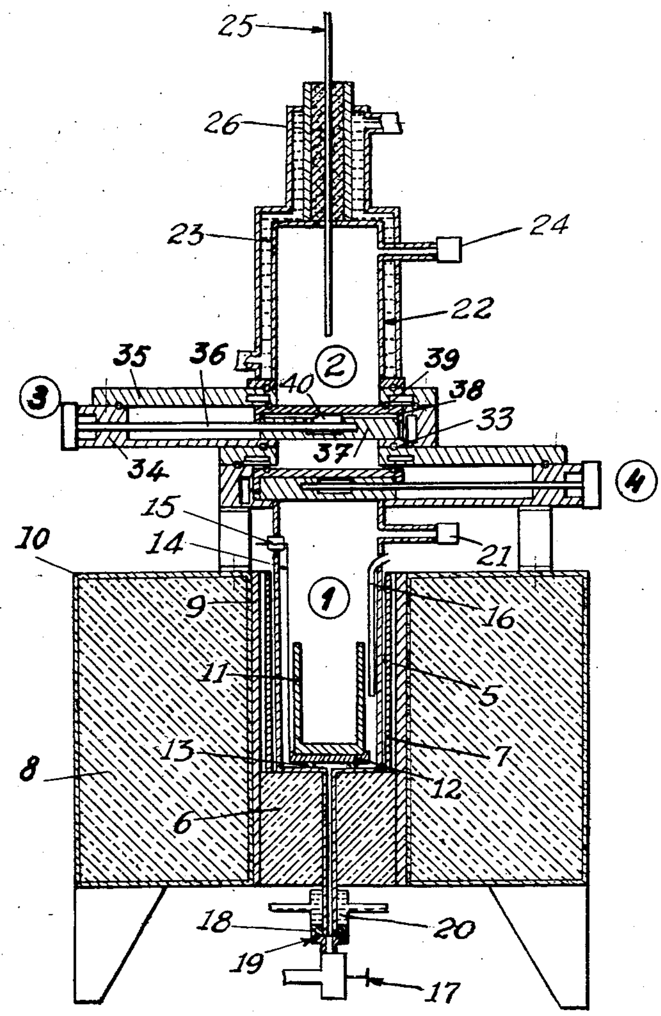
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Fig. 1

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HIGH TEMPERATURE ELECTROLYTIC CELL

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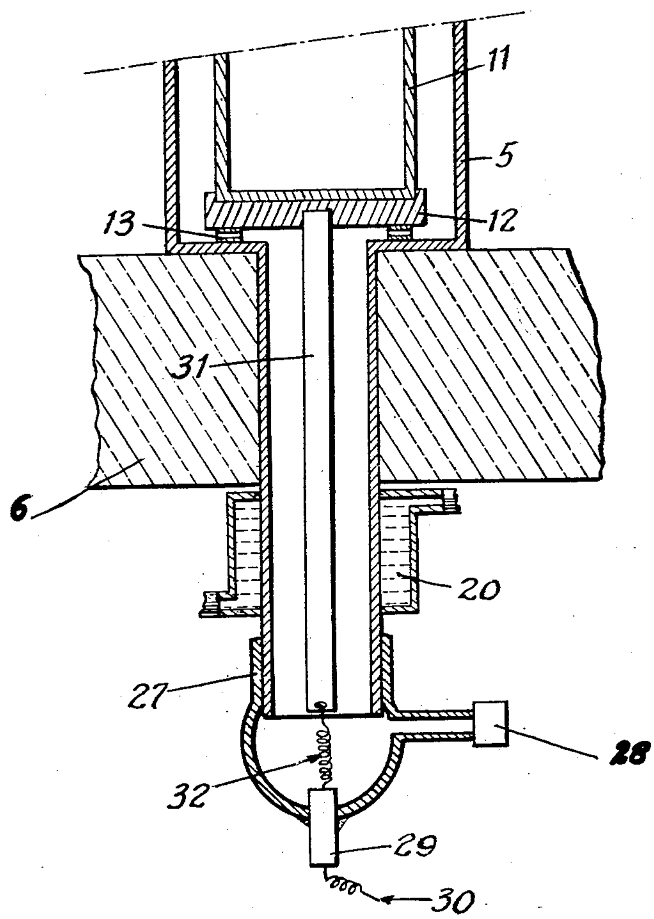

Fig 2

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HIGH TEMPERATURE ELECTROLYTIC CELL

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Claims priority, application France June 7, 1956
2 Claims. (Cl. 204—245)

The present invention relates to electrolytic cells and in particular to cells for the preparation of high purity metals or alloys by electrolysis of salts in the molten state at high temperature.

The chief object of our invention is to provide a cell of this type which permits of easily degassing the vessel in which electrolysis takes place, and possibly the salts which constitute the electrolyte, before electrolysis proper, of performing electrolysis under a vacuum or in an inert atmosphere, and of cooling down the resulting electrolytic deposit under a vacuum or in an inert atmosphere.

According to our invention, the electrolytic cell includes a muffle (intended to receive the treatment crucible) and at least one cooling chamber (for cooling down the treated electrode), this muffle and this chamber being metallic and means being provided for either placing them in communication with each other or separating them from each other, said means including a gastight valve device of the type comprising a sliding unit. Preferably the muffle and the chamber are each provided with such a valve device and they are connected together in detachable manner by a direct and gastight connection between these two valve devices.

It should be reminded that the preparation of high purity metals or alloys by electrolysis of salts in the molten state at high temperature makes it necessary to use a cell capable of complying with the optimum conditions for this preparation, that is to say:

A degassing at high temperature (from 800 to 1000° C. for instance) and in a vacuum (10^{-2} mm. of Hg for instance) of the whole of the cell before electrolysis proper;

An analogous degassing of the salts which constitute the electrolyte (the temperature and pressure conditions being in this case not so rigorous as above);

An electrolysis, and subsequently a cooling, of the electrolytic deposit performed in a vacuum or in an inert atmosphere.

As a matter of fact, the metals or alloys thus prepared must, in order to have good mechanical characteristics, a good resistance to corrosion, a low absorption cross section in the case of nuclear applications, and so on, contain as little as possible of impurities and in particular very low amounts of oxygen and nitrogen. Oxygen is particularly difficult to eliminate.

In order to solve this problem, various types of cells have been used which made it possible to obtain good results. However, their use on an industrial scale involves some important drawbacks.

It is necessary to degas the whole of the system, that is to say the crucible, its supports and the heating elements which are made of graphite and also the materials used for heat insulation (refractory bricks) and for electric insulation (support of ZrO_2); degassing of these porous materials requires relatively powerful pumping means.

Furthermore, if, during an operation, the crucible which contains the electrolyte is broken, the molten salts are spilled in the whole of the cell. It is then necessary to take said cell into parts. Furthermore, recovery of the various constitutive elements into which the solidified salts have been impregnated is difficult. Of course, these elements may be washed but, as they are very porous,

extraction of the salts therefrom is never perfect and these salts may ooze out during the next operation. In this case, it is preferable to change the whole inner structure of the cell, but this is long and costly.

Finally, these known cells made on an industrial scale do not include a cooling chamber.

In order to obviate these drawbacks, according to our invention, the cell is made of two metallic parts, to wit, a muffle and a cooling chamber, each preferably including a gastight valve device of the type comprising a sliding unit, said two parts being connected together through this valve device.

In a preferred embodiment of the electrolytic cell according to our invention, the metallic muffle is vertical. It is heated externally and is insulated either by means of refractory materials or by means of screens and water-jackets. The whole is surrounded by a metallic casing which may be cooled or not. Furthermore, the muffle is provided at its lower part with a valve device making it possible to ensure either gastightness under a vacuum or circulation of a suitable gas through the muffle. This valve device is protected from the hot source.

The cooling chamber, which is also metallic, is cooled down by a circulation of fluid. It is provided at its upper part with a valve device making it possible to ensure either gastightness under a vacuum or circulation of a suitable gas through the chamber. It is further provided with a gastight and insulating passage for the electrode.

At the upper part of the muffle there is provided a gastight sliding valve device which will be hereinafter called the "lower valve device." This device is of the type described in our French patent application No. 715,869 of June 5, 1956.

The chamber has its lower part fixed to another sliding valve device of the same type which will be hereinafter called the "upper valve device."

Such a sliding valve device essentially includes a casing and a sliding unit movable in said casing under the action of an external control member so as to be able either to close or to clear the opening which is to be controlled. The packing joints which achieve gastightness in such a valve are cooled by means of a circulation of fluid in their vicinity, this circulation advantageously taking place in circuits provided in the casing.

The nature of the metals and/or alloys used for the construction of the cell depends essentially upon the temperature to which they are subjected and upon the possible corrosion they may undergo from the gaseous products evolved during electrolysis.

The electrolytic cell according to our invention has many advantages over the known systems.

It is possible, when a suitable deposit has been formed on the electrode, to lift said electrode into the cooling chamber, to insulate it by means of the upper valve device and to remove it without difficulty. This operation permits of cooling down the electrolytic deposit under vacuum or in an inert atmosphere and, during this time, to bring a second chamber into position for a new operation.

As the cell is entirely metallic, it permits:

Of operating at high temperatures, for instance ranging from 1000° to 1200° C.;

Of obtaining pressures ranging from 10^{-4} to 10^{-5} mm. of mercury with pumping means much less powerful than those necessary when this pumping is to be performed in the presence of refractory materials or of graphite, the volumes and surfaces to be degassed being relatively small; as a matter of fact, the volume to be degassed is reduced to that of the metallic muffle and it is not constituted, as in the case of the known cells, by the whole of the apparatus;

Of effecting a periodical cleaning of the apparatus which is necessary in view of the fact that a partial sublimation of the salts and condensation thereof on the cooler portions of the oven takes place during electrolysis. It is possible to perform this cleaning by washing with water without for this reason accepting a higher rate of oxygen for the metal which will be subsequently deposited upon the electrode whereas, in the case of a cell the elements of which are made of graphite or refractory materials, the operation is very delicate because the water absorbed by these porous elements is very difficult to eliminate and constitutes a cause of soiling by oxygen;

Of obtaining metals in which the percentage of oxygen is very low since it has been possible to prepare zirconium containing 0.004% of oxygen, even after washing of the oven with a great amount of water, whereas with an ordinary laboratory cell it is only possible to prepare zirconium containing from 0.5 to 2% of oxygen, although great precautions have been taken in order to avoid soiling either by air occluded in refractory materials or by traces of moisture; with the best cells known at the present time, the rate of oxygen in zirconium can be lowered only to values ranging from 0.04 to 0.2%;

Of quickly remedying a stoppage of the operation caused by breaking of a crucible; as a matter of fact, in this case, molten salts are kept in the metallic muffle and it suffices to unscrew the lower valve device and to clean the muffle with hot water, an operation which is both quick and little expensive.

Preferred embodiments of our invention will be hereinafter described with reference to the appended drawings given merely by way of example and in which:

FIG. 1 is a sectional view of the electrolytic cell according to our invention.

FIG. 2 shows a modification of a part of the cell of FIG. 1.

The electrolytic cell of FIG. 1 includes the oven proper **1**, the cooling chamber **2** and the two gastight valve devices **3** and **4**.

The oven **1** includes a metallic muffle **5** resting upon a support **6** and heated by a heating element **7**. The whole is surrounded by a heat insulating envelope. Advantageously there is mounted between the heating element **7** and the heat insulating envelope **8** a muffle **9** for protection of said envelope. The whole is contained in a metal casing **10**.

Inside muffle **5**, there is provided a crucible **11** which is for instance made of graphite. It rests upon a positioning plate **12** made of a conductor material and resting, through insulating means **13**, upon the bottom of muffle **5**. Current is fed to said plate **12** through a wire **14** which passes through the wall of muffle **5** inside an insulating block **15**.

The temperature inside muffle **5** is indicated by a thermo-electric couple housed in a sheath **16**. A valve device **17** is mounted on the lower end of muffle **5** under support **6** by means of a packaging device **18**, the toroidal joint **19** being protected against the action of the hot source by a water jacket **20**.

At the upper part of muffle **5**, there is provided a valve device **21** which may be cooled in a suitable manner.

The cooling chamber **2** includes a metal envelope **22** cooled by a water-jacket **23** and provided with a valve device **24**. The electrode, in this case cathode **25**, passes through the upper part of said chamber **2**, gastightness being ensured by packing joint **26** which is cooled by water-jacket **23**.

The upper valve device **3** includes a casing made of two portions, the lower one **34** and the upper one **35**, between which can move a sliding unit operated by means of a rod **36** passing through the wall of said casing.

Said sliding unit includes a supporting plate **37** and a cover **38** slidable vertically thereon. This cover **38** can be displaced in a direction at right angles to the direction of movement of the sliding unit so as to ensure a gastight closing of the valve device by crushing of a toroidal joint **39**. This displacement of cover **38** is advantageously obtained by rotation of an eccentric cam **40** rigid with rod **36**.

The packing joints which ensure gastightness between the two portions **34** and **35** of the casing, between the lower portion **34** and the lower valve device **4**, between the upper portion **35** and cooling chamber **2**, and also joint **40**, are preferably toroidal and are cooled by circulation of fluid in their immediate vicinity, this circulation taking place through a circuit preferably provided in the walls of the casing.

The lower valve device **4** is made similarly.

These valve devices achieve a very good gastightness even when they are subjected to the action of high temperatures; they are strong, easy to operate and permit of quickly obtaining great areas of opening.

The upper valve device **3** is shown in closed position with its cover **38** applied against the upper casing portion **35**. The lower valve device **4** is shown in closing position but with the cover of its sliding unit loosened.

FIG. 2 shows a modification of the device for feeding current to positioning plate **12** on which crucible **11** is resting. The metallic muffle **5** carries at its lower end, beyond the cooling jacket **20**, a gastight chamber **27**. This chamber is provided with a valve device **28** and insulating means **29** for the passage of an electric conductor through the wall of said chamber; electric connection between plate **12** and conduct **30** is ensured by means of a contact rod **31** rigid with plate **12** and a flexible wire **32**.

With the cell described in reference to FIGS. 1 and 2, electrolytic preparation of high purity metals or alloys takes place as follows:

Cooling chamber **2** having been previously removed, valve device **4** is opened by rotating rod **36** through an angle of 90° and then pulling said rod outwardly.

Crucible **11**, for instance of graphite, which is to be degassed is introduced into oven **1**. Valve device **4** is closed by pushing in rod **36** and rotating it about its axis through an angle of 90° in a direction opposed to that of the above mentioned rotation of said rod.

Valve device **17** is closed and the desired vacuum is produced in oven **1** by pumpng out the air present therein through the valve device **21**; the oven is heated and degassing is performed at the desired temperature and pressure. When a sufficient degassing has been obtained, atmospheric pressure is restored by introducing an inert gas through valve device **17**. This gas will be evacuated through valve device **21** or possibly through valve device **4**.

The salts are introduced into crucible **11**, for instance through the opening of valve device **4**, this operation being effected quickly and smoothly so as to introduce the minimum amount of air into the muffle. The salts are then melted in an inert atmosphere or under vacuum. In the latter case, and when it is desired to degas the salts preliminarily under vacuum without waiting for their being melted, the operation is identical to the above described degassing operation.

The salts being in the molten state, the atmosphere inside the oven is constituted by an inert gas, this gas entering through valve device **17** and issuing through valve device **21**, sliding valve device **4** being closed.

The cooling chamber **2** is then fitted as shown by FIG. 1, the upper electrode **25** (in this case the cathode) being in position. Screws, not visible on the drawing, permit of securing valve device **3** to valve device **4**, gastightness being ensured by toroidal packing joint **33**. Chamber **2** is degassed, if so desired, through valve device **24**, after which an inert atmosphere is provided in said chamber.

Valve devices **3** and **4** are opened. The valve device **21** of the muffle is closed and the valve device **24** of the chamber is opened. The gas entering through valve device **17** therefore flows out through valve device **24**, free passage being provided between oven **1** and chamber **2**.

Cathode **25** is lowered and electrolysis is performed either in a vacuum or in an inert atmosphere.

After electrolysis, cathode **25** with its deposit is lifted into the cooling chamber **2**. Sliding valve device **3** is closed. The deposit is left to cool down either in an inert atmosphere (possibly with a light over-pressure), valve device **24** being closed, or in a vacuum.

During this time, valve device **4** has been closed and valve device **21** opened to permit gas circulation. Chamber **2** is then removed and replaced by another chamber if so desired.

All these operations can be performed quickly without difficulty. They can be made in at most fifteen minutes both before and after electrolysis proper.

In a general manner, while we have, in the above description, disclosed what we deem to be practical and efficient embodiments of our invention, it should be well understood that we do not wish to be limited thereto as there might be changes made in the arrangement, disposition and form of the parts without departing from the principle of the present invention as comprehended within the scope of the accompanying claims.

What we claim is:

1. An electrolytic cell comprising a metallic muffle, an electrically conductive crucible in said muffle spaced

from the walls of said muffle and electrically insulated therefrom, means for heating said muffle, means for electrically heating said crucible, a cooling chamber removably mounted above said muffle, said cooling chamber having an opening at the lower end thereof located above the top end of said crucible, gastight valve means interposed between said muffle and said chamber for either placing them in communication with each other or separating them from each other, said valve means including a gastight valve device carried by said muffle at the top end thereof to control the opening thereof, the valve opening being of such size as to allow introduction and removal of said crucible, a gastight valve device carried by said cooling chamber at the lower end thereof to control the opening thereof, gastight means joining said two valve devices, and an electrode mounted on said cooling chamber and vertically slidable therein for lowering into said crucible when both said valve devices are open.

2. An electrolytic cell as claimed in claim 1, wherein said gastight means include a toroidal packing joint and fluid circulation means for cooling said joint.

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