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ELECTROLYSIS OF RARE-EARTH ELEMENTS AND YTTRIUM

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This invention relates to the electrolytic production of yttrium and metals of the rare-earth group (atomic numbers 59 through 71) from their respective halides or oxides.

The object is the commercially practical electrolytic production of these metals and alloys thereof in highest purity responding to the most exacting requirements and heretofore industrially unattainable. The processing is continuous and the resultant purity in excess of 99.9% and there is substantial freedom from non-metallic impurities such as oxides, carbon, carbides, nitrogen, nitrides and the like.

Yttrium has been prepared by electrolysis and by calcium reduction with and without the use of boosters and with and without the use of slagging agents. Metal produced by such methods is not of high purity due to the difficulties encountered in separating the metal product from the electrolyte, reductant and slag, and the obstacles are increased with the higher melting members of the group.

As applied to yttrium, for instance, matters still unresolved electrolytically may be exemplified by a novel processing with full precautionary purifying and intricate manipulative procedures and controls as follows:

EXAMPLE A

The YCl_3 (99.9+ % purity) was prepared by dissolving Y_2O_3 in concentrated HCl and evaporating the solution under a dry HCl gas atmosphere to dryness. The YCl_3 was slowly heated to within $50^\circ C.$ of the melting point under a dry HCl gas to remove the last water of hydration. The anhydrous salt was stored in a desiccator under inert gas. LiCl was purified and dehydrated by fusion under dry HCl gas, fused, and HCl gas bubbled through the melt to remove residual moisture.

Three parts of the YCl_3 were fused with one part of the LiCl under a dry HCl atmosphere in an inert cell. Pure dry HCl gas was bubbled through the melt to decompose carbonates, sulfates and the like and to remove any residual moisture. The electrolyte and the interior of the cell were purged of HCl gas by pumping dry pure argon gas through the cell.

The interior of the cell was maintained slightly above atmospheric pressure throughout the course of the run by the inflow of dry pure argon. The temperature was maintained at $850^\circ C.$ A nickel cathode was lowered into the electrolyte and positioned close to the bottom of the insulated cell. A parallel graphite anode was lowered into the electrolyte at another point so as to have the cell in the usual anode and cathode sections.

Electrolysis was commenced at first at low impressed voltage to rid the bath of baser metal impurities and later at high voltage to deposit Y metal at the cathode. The first deposits were discarded. The anode current density was maintained below 7 amperes per square inch during the process electrolysis and the initial cathode current density was about 40 amperes per square inch. The impressed voltage was about 6.2 volts and about 20

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amperes were passed through the cell for about four hours.

At the end of this run, the cathode and its adherent deposit were withdrawn into the argon atmosphere about the cell and allowed to drain free of the electrolyte. The cathode and the deposit were then allowed to cool to room temperature before removal in a dry box. The cathode tip was physically separated from the deposited metal and salt. The metal crystals and salt were transferred to an extraction apparatus where the salt was leached from the metal crystals by pyridine purified and dehydrated over pure lithium metal. The yttrium crystals were well-formed and silvery white in color. The crystals were consolidated by fusion under high vacuum.

All of this severely restricts the applicability of the electrolyzing procedure and renders it relatively expensive and troublesome, and further problems arise specifically in connection with the individual metals of the rare earth groupings as indicated briefly in Table 1 below:

Table 1

Element	Recorded M.P., ° C.	Solubility	Lacking in Adaptability
La	835±15	No	A, B.
Ce	793± 5	No	A, B.
Pr	950±10	Some	?
Nd	820±10	Some	?
Sm	1,350 (?)	Yes	C.
Eu	1,150±50	No	C.
Gd	1,350 (?)	Solubility varies widely from little to none at all.	C and/or B.
Tb	1,450±50		C and/or B.
Dy	1,500 (?)		C and/or B.
Ho	1,500 (?)		C and/or B.
Er	1,525±25		C.
Tm	1,600±50		C and/or B.
Yb	824 (?)		C.
Lu	1,700±50		C and/or B.

A—Low melting point, metal fog, etc.

B—Reactivity with salt solvents.

C—Multiple valency.

Solubility refers to the solubility of the respective chloride in anhydrous pyridine.

Of these possibly praseodymium or neodymium may be adaptable to the above processing, but elements such as cerium have too low melting points (condition "A") and are simpler to recover in the fused or consolidated state. However, the recovery of other rare-earth metals in the fused state is not undertaken due to (1) the high melting points, above $1000^\circ C.$ for most of the metals; (2) the high vapor pressure of the respective halides of the metals at the temperature of fusion resulting in low physical stability and high losses; and (3) the high reactivity of the electrolyte with the deposited metal and materials of construction.

These elements, in the highly pure state, are very reactive with water and common solubilization media so that the metals are not readily separated from their adhering electrolyte by fusion of the metal or solution of the salt in an inert solvent (condition "B"). That is, inasmuch as the metals must be deposited below their melting points, those elements which cannot subsequently be separated from the adhering salt by gravity on fusion at low temperature must have halide salt solubility in an inert solvent such as moisture-free pyridine.

Some of the metals like Sm and Eu manifest multiple valencies (condition "C") and on electrolysis deposit only lower valent halide, or at high cathode current densities deposit metal contaminated by both lower valent halides and the solvent metal by co-deposition. In addition, it has been demonstrated that electrolysis of the rare-earth halides (or mixes with oxides) alone results in the formation of metal fog due to the high solubility of these metals in their respective halides. This phenomenon is aggravated by elevated temperatures. Also,

the expedient of reducing metal fog by the introduction of alkali and/or alkaline earth halides represents a false solution in that only lithium chloride is readily removable from the electrodeposited metal by means of a solvent inert to the metal. Further, it has been shown that these rare-earth metals are extensively electropositive and at high temperatures can reduce alkali and alkaline earth halides to metal. Consequently, it is imperative that the concentration of the diluent solvent alkali and/or alkaline earth halides be neither too high nor too low. For if the concentration be too high, co-deposition will take place, and contrariwise, if the concentration be too low, there will be excessive metal loss due to metal resolution in the electrolyte and due to the deposition of lower valent halides in the case of the multivalent members of the group.

To solve these difficulties and make the high purity metals practically available the present processing passes the metal through a molten alloy stage combining with a special electrolytic supply to receive therefrom metal deposit at one section and then acting as an anode source of purified metal for another electrolyte at a second section.

In the two stage processes of the invention, the respective rare-earth halide or oxide is electrolyzed as solute under an inert gas atmosphere in a bath containing between two moles and four moles of the solute to one of the solvent diluent alkali and alkaline earth halide. The anode can be carbon or graphite and the current density should not exceed about 10 amperes per square inch. In this stage of the process, the preferred range of anode current density is between 3 and 7 amperes per square inch at the liquid metal electrode. Only those alloying elements which are less electropositive than the respective rare-earth metal with respect to halogen are selected and it is important that the liquidus temperature of the lowest melting eutectic be substantially below, for instance at least 100° C. below, the melting point of the pure rare-earth element. Among the alloying elements which can be utilized are Cu, Ag, Au, Zn, Cd, Sn, Sb, Si and the like. However, the liquid alloy eutectic compositions with copper are preferred. These alloys are liquid at least 100° C. below the melting temperature of the pure rare metal, and more important the atomic ratio of the rare metal to that of Cu in the alloy is greater than 1:2 and usually greater than 1:1 and even greater than 2:1.

The cathode liquid alloy must contain a substantially quantity of rare metal in solution. Otherwise it is not possible to effectively deposit the rare metal in the alloy. For example, it is difficult to electrodeposit those rare metals in a liquid cathode which is free or has little of the rare-earth element dissolved therein. With the multivalent elements, the lower valent halide usually appears and in other circumstances a hard crust forms on the surface of the denser liquid cathode which causes the process to fail. However, by using a lower melting eutectic containing a substantial quantity of dissolved rare-earth metal, on electrolysis the metal is deposited on and in the liquid alloy where it is rapidly accepted, assimilated, dispersed and distributed throughout the alloy due to the electromagnetic fields set up in the cell and to the chemical and physical character of the alloy electrode.

For similar reasons, it is best to maintain the rare metal solute in the electrolyte fairly constant by the continuous addition of anhydrous chloride or oxide to the bath. The solvent salts are selected from the alkali and alkaline earth halides but for convenience, for cheapness and ease of operation the chlorides and fluorides are preferred. Eutectic compositions have advantageous properties and are preferred. The use of alkali (with or without alkaline earth) metal halides is restricted to the use of the rare-earth metal halide. The rare-earth metal halide solute may be the lower valent or subhalide, and the chlo-

rides are preferred although the fluorides may also be used. The bromides and iodides are expensive. The molar ratio of these rare metal halides to that of the solvent halides, in this invention, can be varied over a remarkably wide range without impairing the quality of the product. However, it is preferable to maintain the molar percentage from about 10 to 75 percent. In this way, the liquidus temperature can be regulated to conform with the limits set by the alloy eutectic liquid temperatures. Other things being equal, the high molar percentages are preferred. For example, a 35 mol percent is preferable to a 10 mol percent solution.

In place of the rare-earth chloride it is possible to feed the cell electrolyte with the rare metal oxide. Again, the lower valent oxides may be used; though the solubility of these oxides in the solvent is usually quite low, I find it may be improved by the addition of the respective rare metal fluoride. The oxides have the advantage of lower cost and obviate the nuisance of arduous dehydration of the halides of the rare-earth elements. The solvent salts are restricted to the alkaline earth halides with an oxide feed. Again, the fluorides and chlorides are preferred.

The temperature of the bath and the alloy should be at least 50 to 100° C. above the liquidus temperature of the bath. The composition of the electrolyte can be varied within the range described to produce a low melting eutectic bath or mixture. In any event, the electrolyte is compounded so that its liquidus temperature is below that of the alloy.

The liquid alloy cathode current density can be varied over a wide range without adversely affecting the nature of the electrolysis. The best results are obtained at the higher current densities, i.e., in excess of 50 amperes per square inch. However, as dictated by the geometry of most usable electrolytic cells, current densities of 10 amperes per square inch and less may be used.

An illustration of this phase of the process is given in Example I.

EXAMPLE I

Fused an eutectic mixture of 80 LiCl and 20 LiF under an inert gas atmosphere in a sealable furnace lined with a graphite crucible which subsequently was used as the anode. The temperature was raised to 650° C. and pure anhydrous CeCl₃ was added to the bath until about 15 mol percent had been added. An eutectic alloy of 15 Cu—85 Ce (which fuses at about 415° C.) which had been prepared by chemical reduction was added bit by bit to the electrolyte. The alloy fused and formed a mobile liquid layer at the bottom of the cell. A graphite anode was lowered into the electrolyte and electrolysis commenced. During the course of electrolysis the chlorine gas produced at the anode was swept from the cell by the continuous inflow of pure dry argon. Also during the passage of the current through the cell, pure anhydrous CeCl₃ was continuously fed to the catholyte electrolyte so as to maintain as constant a concentration as possible. The electrolysis was continued for about four hours at about 100 amperes. At the end of the run, the anode was slowly withdrawn from the electrolyte. The alloy was sampled and analyzed. The remainder of the alloy was subsequently refined. The results are summarized in Table 2.

Table 2

Duration of run, about.....	400 amp. hrs.
Temperature.....	625° ± 25° C.
Concentration, CeCl ₃ calc.....	15 ± 3 mol percent.
Anode current density.....	6.3 amp./inch ² .
Cathode current density.....	10.6 amp./inch ² .
Concentration Ce at start.....	84.1 w/o.
Concentration of Ce at end.....	88.7 w/o.

All of the rare-earth metals and yttrium may be electrolyzed in the same fashion to produce a copper alloy. Whatever the reason, in this way the characteristic of multiple valency does not confound the electrolysis and

all of the elements of the group are equally well deposited at high efficiency in the liquid alloy cathode. In this first stage it is apparent that purification of the rare metal is already taking place in that more electropositive elements are not co-deposited. Also, for some reason, the alloys may be kept operative in graphite lined crucibles. Other materials, such as ceramics, are rapidly attacked by the fluid alloys and should be avoided. Tantalum has been found to serve satisfactorily as a container material.

The alloys are then processed by making them the anode in a refining electrolytic cell, under an inert gas atmosphere. The temperature of the alloy is maintained as before at about 50 to 100° C. above its liquidus temperature to insure adequate mobility of the liquid alloy electrode. The electrolyte in this part of the process is composed of alkali and/or alkaline earth halides only and must be free of oxides of any kind and moisture. Although any of the halides are useful, the bromides and iodides are costly; the fluorides make better fluxes, but are higher melting and boiling than the chlorides which are preferred. The electrolyte solute, i.e., the rare metal halide (again preferably the chloride) must be anhydrous and oxide-free. The concentration of these solutes in this invention may be varied over a wide range without adversely affecting either the workability of the process or the purity of the electrolytic product. The optimum concentration is determined principally by (1) the subsequent operations to which the product will be put, and (2) the melting point of the rare-earth metal deposited. Within this limitation, the concentration may be varied between a few mol percent to over 80 mol percent. However, in order to restrict the drag-out salt recovery problem, it is preferable to maintain the solute concentration below 50 w/o but above 10 w/o. The higher concentrations are preferred for the high atomic weight metals of the group. In practice, a routine test will determine the optimum concentration. Actually, the quantity of drag-out will usually be very low as the salts will, for the most part, run off the deposited metal into the bath as the depositing metal is slowly withdrawn from the electrolyte during electrolysis in order to (1) maintain a nearly constant high cathode current density, (2) remove the deposit from the area wherein secondary chemical reaction with the electrolyte may occur, and (3) preserve the unique and highly desirable physical character of the deposit. It should be remembered that the invention depends on the deposition of the rare-earth metal in a solid state. Therefore, the electrolyte is formulated so as to manifest a low liquidus temperature.

The liquid alloy current density is maintained below about 10 amperes per square inch in order to insure a high purification of the product. Although the anodic current density may be varied from a few tenths of an ampere per square inch to about 25 amperes per square inch, I prefer to limit the current density at this electrode to 5 to 7 amperes per square inch.

The cathode current density may be varied over a wide range without impairing the product purity or the operability of the process. However, the higher current densities between 25 and 75 amperes per square inch are preferred, and successful operation has been had between a few amperes to over 600 amperes per square inch. At the higher current densities, the cathode requires cooling.

The material of the cathode must not be composed of any material which will alloy or react with the depositing metal and at the same time, in order to achieve adherence to the cathode, conductors such as tantalum cannot be used as these metals do not appear to "wet" such materials. I prefer, therefore, to use the metal being deposited as a cathode tip, and if required to cool the cathode and its lead to prevent union or reaction with the tip.

The temperature of the bath is determined essentially by the liquidus temperature of the alloy anode. The temperature should be kept as low as practicable to prevent

adverse reactions and should be about 50 to 100° C. above the liquidus temperature of the alloy.

An illustration of the operation of this part of the process is given in Example II.

EXAMPLE II

In a thoroughly dried electrolytic cell under a dry pure argon gas atmosphere fused at about 650° C. a eutectic mix of 59 LiCl—41 KCl (melting point about 350° C.) which had been dehydrated under dry HCl gas. The eutectic mix was further purified by bubbling HCl through the melt. Pure dehydrated CeCl₃ was added to the melt to make about 7 mol percent solution as calculated. An alloy of 85 Ce—15 Cu was added to the bath. The alloy melted and formed a liquid anode at the bottom of the inert crucible liner. A water cooled nickel cathode was lowered into the electrolyte and the electrolysis was commenced. Shortly after the start of electrolysis, the cathode was slowly withdrawn from the electrolyte so that a relatively constant current density was maintained thereat. After about three hours of deposition, the cathode was withdrawn into the inert space above the electrolyte and allow to drain free of salts. The tip of the cathode and its adherent deposit and salts was transferred to a vacuum furnace where the Ce was separated from the salts by fusion. The metal was in excess of 99.9% pure and substantially free of non-metallic impurities. The operating statistics are summarized in Table 3.

Table 3

Duration of electrolysis, about-----	150 amp. hrs.
Temperature -----	625 ± 25° C.
Concentration, CeCl ₃ , calculated-----	6.8 M percent.
Anode Current Density-----	5.3 amp./inch ² .
Initial cathode current density-----	29.4 amp./inch ² .
Concentration Ce in alloy at start----	88.7 w/o.
Concentration Ce in alloy at end-----	87.0 w/o.
Purity of recovered Ce metal-----	99.9+ percent.

The liquid alloys of the rare-earth elements and yttrium can be refined in a similar fashion with the production of a solid pure product at high current efficiency. Although I do not wish to be committed to any theory and can only report the results of my invention, the successful practice of this invention is intimately bound to the nature of the crystalline product that is deposited and formed from an electrolyte containing the respective rare metal chloride and cations more electropositive than the respective rare metal with respect to halogens when there is a liquid anode containing a substantial amount of the rare metal dissolved in a metal less electropositive than the respective metal with respect to halogens. The electrolyte is stable physically and chemically. The rare metal under the influence of the electric current is preferentially and selectively dissolved from the liquid alloy and enters the electrolyte. At the cathode, the rare-earth metal is deposited in an exceedingly pure form as a well defined crystal.

Although the process has been illustrated in two steps or phases, the process is best practiced as a single one cell operation, the results obtained therefrom being outstandingly superior and advantageous. In a single cell, wherein a single liquid alloy electrode serves as the cathode in the reductor side of a compartmentalized cell and as an anode in the refining section, not only is the character of the product enormously more suited to higher purity and efficiency due to the continuous operation of all components of the process, i.e., the two diverse electrolytes, the liquid bipolar electrode, the current flow, etc. always at an optimum, but the cell is easier and simpler to operate. In addition, many of the practical problems associated with the intermittent processing are obviated. The simple cell design admirably lends itself to large scale production with a minimum of supervision and labor.

An illustration of the operation of the process in a single bipolar cell is given in Example III.

EXAMPLE III

A cell divided into two compartments by a dependent baffle terminating within two inches of the bottom of the cell was carefully dehydrated by heating the cell under a vacuum. The cell was alternately filled with pure dry argon and evacuated to purge the cell of air. The interior of the cell was finally maintained under a dry purified argon atmosphere at slightly above atmospheric pressure. Via a gas lock-feed port in the reductor section of the cell, an alloy of Cu and Y was fed in small amounts, allowing each to melt before adding the next. In this way, a three inch depth of alloy was generated effectively sealing off and isolating the two compartments from each other. The alloy was prepared by the chemical reduction of YCl_3 and $CuCl_2$ by pure redistilled calcium. The temperature was about $950^\circ C$. The anolyte or reductor section was filled to a height of about 4 inches with a carefully purified anhydrous electrolyte composed of 60.8 w/o $CaCl_2$ —10.5 w/o CaF_2 —3.5 w/o YF_3 —25.2 w/o YCl_3 . The graphite anodes were immersed about one inch. During the course of electrolysis, pure anhydrous YCl_3 was continuously fed to the electrolyte to synchronize with the rate of electrolytic decomposition of the YCl_3 to Y metal alloy and Cl_2 . The chlorine gas was continuously swept from the anode compartment by purified argon gas leaving the cathode chamber, which was at slightly higher pressure.

The catholyte or refining section was filled to about 4 inches with a purified anhydrous melt composed of 76.3 w/o $LiCl$ and 23.3 w/o YCl_3 . Pure dry argon gas entered the chamber and passed through to the anolyte chamber. During the course of electrolysis, the cathode and its adhering deposit was gradually withdrawn from the electrolyte so as to prevent short circuiting of this compartment and in an attempt to maintain a more uniform high current density.

A 50 ampere D.C. current was passed between the graphite anode and the solid cooled cathode. After about 4 hours, the cathode was withdrawn and allowed to cool, the cathode tip and its adhering deposit and residual salts were replaced by a new tip and the electrolysis recommenced. The YCl_3 was fed to the anolyte at the rate of about $\frac{1}{4}$ pound per hour.

The deposit and the adhering salt was scraped into a retaining extraction thimble in a dry box and the salts were leached from the metal crystals by anhydrous pure pyridine that was continuously treated with pure lithium metal pellets. The recovered metal was in the form of large silvery crystals deposited one on top of the other and in a dense matrix that seemed to have undergone extensive diffusion or incipient fusion. No discolored dark metal or powder was found. The cleansed metal was readily fused into an ingot in a vacuum furnace. It remained silvery bright but had to be stored under an inert water-free hydrocarbon to prevent discoloration or reaction with moisture. The operating characteristics are summarized in Table 4.

Table 4

Graphite anode current density	6.5 amp./in. ²
Liquid alloy cathode current density	15.9 amp./in. ²
Liquid alloy anode current density	7.0 amp./in. ²
Initial cathode current density, calculated	29.4 amp./in. ²
Purity of Y product	99.9+ percent
Composition of alloy 30 Y—70 Cu calculated.	

EXAMPLE IV

A cell identical to that used in Example III above was used for the preparation of high purity cerium metal, except that the cerium stripped from the cathode tip was not treated with pyridine, but separated from the salt electrolyte by vacuum fusion. The metal was silvery

bright and of high purity. The operating data is summarized in Table 5.

Table 5

5	Duration of run (50 amperes)	5 hours.
	Temperature of bath approx.	$550^\circ C$.
	Composition of anolyte	66.6 $LiCl$ 16.7 LiF 16.7 $CeCl_3$
10	Composition of catholyte	49.1 $LiCl$ 34.2 KCl 16.7 $CeCl_3$
	Rate of Feed — $CeCl_3$ — about	0.6 lb./hr.
	Liquid alloy composition	85 Ce —15 Cu
15	Graphite anode current density	6.5 amp./in. ²
	Liquid cathode current density	15.9 amp./in. ²
	Liquid anode current density	7.0 amp./in. ²
	Initial cathode, solid, current density	29.4 amp./in. ²

Having described in considerable detail the practice of the process of the invention, it will be readily apparent that numerous variations and modifications may be made of some of the specific details described herein without departing from the spirit and scope of the invention as defined in the following claims.

I claim:

1. A method for the production of a metal of high purity of the group of rare-earth metals and yttrium comprising, providing a mass of molten alloy of said metal with a relatively minor proportion of solvent metal more noble with respect to halogens and which mass is in surface contact as cathode at one portion with a molten anolyte electrolyte formed by a compound of the group consisting of the oxides and halides of said rare-earth metals and yttrium dissolved in at least one solvent metal halide whose cations are less noble than those of the said rare-earth metals and yttrium with respect to the anions contained in said anolyte electrolyte, said mass of molten alloy being brought into another surface contact with a catholyte electrolyte oxide and oxygen free and consisting of at least one solvent chloride of the group of metals whose cations are less noble than those of said rare-earth metals with respect to chlorides and containing at least one solute chloride of the group of rare-earth metals and yttrium, and electrolyzing said anolyte electrolyte and molten alloy and catholyte electrolyte in series between an anode in contact with said anolyte electrolyte and a cathode in contact with said catholyte electrolyte, and selectively and preferentially dissolving said rare-earth metal from said liquid alloy electrode acting as an anode and depositing said metal of the group of metals of rare-earth metals and yttrium on a solid cathode immersed in said catholyte electrolyte in the form of large crystals of high purity.

2. A method for the production of a metal of the group of rare-earth metals and yttrium as set forth in claim 1 wherein said electrolysis is conducted beneath an inert gas atmosphere.

3. A method for the production of a metal of the group of rare-earth metals and yttrium as set forth in claim 1 wherein the solute in the catholyte electrolyte is selected from the halides of said group of rare-earth metals and yttrium.

4. A method for the production of a metal of the group of rare-earth metals and yttrium as set forth in claim 1 wherein the catholyte electrolyte is oxygen and oxide-free and comprises chlorides.

5. A method for the production of a metal of the group of rare-earth metals and yttrium as set forth in claim 1 wherein said feed to said anolyte electrolyte is selected from the oxides of said group of rare-earth metals and yttrium.

6. A method for the production of a metal of the group of rare-earth metals and yttrium as set forth in claim 3 wherein said solute is the chloride.

7. A method for the production of a metal of the

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group of rare-earth metals and yttrium as set forth in claim 1 wherein said liquid alloy metal solvent comprises copper.

8. A method for the production of high purity yttrium metal comprising electrolyzing a fused bath composed of yttrium chloride and lithium chloride between an anode and a solid inert cathode, thereby depositing yttrium metal on said cathode, subsequently separating said yttrium metal from said adhering chlorides by leaching with anhydrous pyridine.

9. A method for the production of high purity yttrium metal in excess of 99.9% as set forth in claim 8 wherein said anode is a soluble anode.

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10. A method for the production of high purity yttrium metal as set forth in claim 8 wherein said anode is an insoluble anode.

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