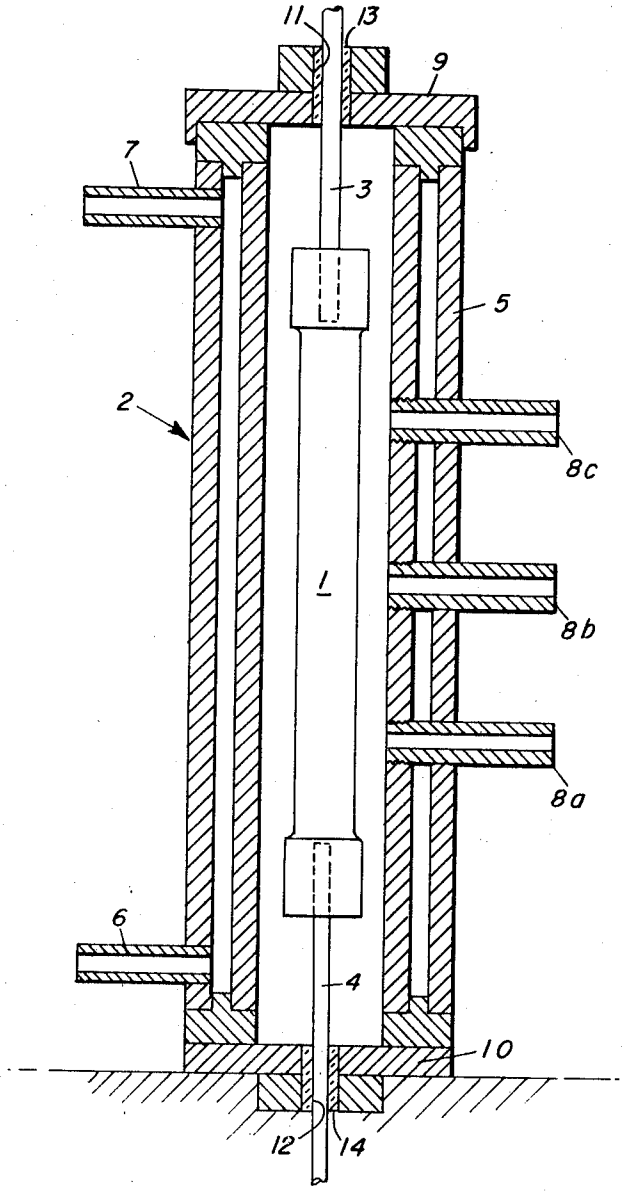
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PURIFICATION OF REACTIVE METALS

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PURIFICATION OF REACTIVE METALS

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ABSTRACT OF THE DISCLOSURE

Reactive metals, such as rare-earth metals, are purified by electrotransport in a pulsed direct current electric field.

This invention relates to the production of reactive metals in a state of high purity. The process of the invention is particularly applicable to rare-earth metals. However, it may also be used to purify other reactive metals such as uranium, thorium and titanium. Rare-earth metals, e.g., cerium, lanthanum, dysprosium, gadolinium, samarium, yttrium, etc. and their compounds are useful in a wide variety of applications such as electronics, phosphors and lasers.

The rare earths are, however, difficult to prepare in a state of high purity by conventional means, such as electrowinning, because of their relatively high melting points and because in the molten state they react with most materials. However, by preparing an alloy of the rare earth and a suitable metal, such as iron, nickel, cobalt, chromium or manganese, the melting point of the electrowon product can be reduced substantially. At the lower temperature, the product is easily electrowon and has a very small interstitial impurity content. For this reason, electrowinning of the alloy to produce a high purity metal with respect to other elements in a relatively simple process. Removal of most of the alloying metal from the product is possible by conventional methods such as vacuum distillation. Only electrotransport, however, is effective in removing small amounts of alloying metal. Similarly, electrotransport is effective in removing small amounts of impurities from any impure reactive metals.

Electrotransport, i.e., the application of an electric field to a solid or liquid metal alloy to cause redistribution of the component elements, has been the subject of many investigations. A general review of its experimental and theoretical aspects is given in an article entitled "Electrotransport as a Means of Purifying Metals" by J. D. Verhoeven, in Journal of Metals, January 1966. When an electric field is applied to a metal or alloy bar, a small percentage of the current is carried by ionic migration. In alloys, ions of one of the component metals may react more strongly to the electric field than other components. As a result, migration may be at a higher rate and of a different direction than the other metals. If the field is applied for sufficient times, separation of the components may occur with migration of impurity atoms to either the anode or cathode end of the metal bar. The separation will continue until back diffusion (chemical potential diffusion) rate equals directed diffusion (electrotransport, electromigration) rate. However, conventional solid state-electrotransport, procedures have generally been relatively inefficient since the field intensity (voltage per unit length), and the resulting current, was limited by the heat developed in the metal as a result of the current flow. It is essential that the rate of heat input, resulting from the current flow, be limited to an equivalent heat output of the metal; otherwise, the metal will overheat and melt. Most prior art processes have used small diameter wires

in order to enable the use of a higher field strength. It is apparent, however, that this procedure is self-defeating because of the difficulty of obtaining the purified products in sufficiently large quantities.

It has now been found, according to the present invention, that the disadvantage of the prior art processes can be largely overcome by employing a pulsed electric field, with resulting pulsed direct current flow in the solid metal to be purified. The use of a pulsed current permits application of substantially higher field strengths and higher currents without overheating the metal. This enables migration and consequent removal of some impurities that cannot be removed by means of steady current flow. Furthermore, the use of the higher pulsed current generally enables more rapid removal of impurities than the use of the lower current values that can be used when a steady state current is employed.

The process of the invention is carried out in conventional apparatus in which the metal to be purified is supported by two leads. This arrangement provides minimum contact between the metal and the container in which the metal is located. These leads consist of inert conductive metals such as molybdenum, tungsten or tantalum. An inert atmosphere such as helium or argon is maintained within the container during the purification process.

As stated above, one of the chief advantages of the process of the invention is that it enables the purification of relatively large metal samples, e.g., bars of from about 4 to 8 inches in length and having diameters of from about ⅜ to ½ inch may generally be purified by the process of the invention. Maximum size, however, will vary considerably with the type of metal to be purified, type and amount of impurity, desired degree of purification, temperature of the sample, etc.

The optimum magnitude and wave form of the electric field applied to the sample, and the resulting current and temperature, will also vary widely depending on the above variables and are best determined empirically. The electric field and current may consist of pulses separated by periods during which the field is removed, or the pulses may be superimposed on a steady d.c. field. The exact wave form of the pulse is generally not critical, provided the magnitude and frequency of the pulses is sufficient to provide a current sufficient to effect the desired purification. The pulsed field may be generated by any conventional means, which will be apparent to those skilled in the art.

A suitable apparatus for use in the process of the invention is illustrated in the figure. This apparatus is, however, conventional and many modifications will be apparent to those skilled in the art. Referring to the drawing, sample **1** (the metal to be purified) is supported in container **2** by means of anode lead **3** and cathode lead **4**. Container **2** consists of water-cooled jacket **5** with water inlet **6** and outlet **7** and thermocouple wells **8***a*, **8***b* and **8***c*. The ends of the container are closed by stainless steel lids **9** and **10** having holes **11** and **12** and ceramic insulators **13** and **14** for insulation of leads **3** and **4** from the container.

The following examples will serve to more particularly illustrate the invention.

EXAMPLES 1–27

In these examples bars of cerium and lanthanum, 6 inches long and ½ inch in diameter, were electrolyzed in steady currents versus pulsed currents for comparison. Molybdenum rods were used as leads to contact the cerium and lanthanum bars. The cross sectional area of the molybdenum was such that the resistance was equal to the cerium and lanthanum; therefore, the molybdenum rod was at very near the same temperature as the bar. A water-cooled copper jacket surrounded the bar to remove

heat as rapidly as possible. Either pulsed or steady direct current was applied to the bar. The temperature was maintained constant at 600° C. for all experiments. Helium gas at atmospheric pressure was used to protect the bar from oxidation. The entire system was contained in an air tight chamber. The pulsing of the current was accomplished by mechanically turning a rectifier off and on through a rotating switch. The switch turned at 60 r.p.m. and the "on time" was about 1/10 the cycle. An oscilloscope was used to analyze the character of the pulse. The voltage and amperage profile were nearly identical indicating that the resistance was nearly independent of the field strength.

Tables 1, 2, and 3 show the operating conditions and results of two similar cerium or two similar lanthanum bars. The initial impurity concentration was uniform throughout the bar length. The impurity content values for the anode and cathode are from analyses made after the electrolysis. These results show that molybdenum did not migrate in a steady current while the pulsed current caused significant electrotransport of molybdenum as indicated by the content at the cathode being six times that at the anode. The pulsed current also had a strong effect on the migration of copper, oxygen, and manganese. At the same time, there was no improvement on the migration of iron impurities in cerium but some improvement in iron migration in the lanthanum bar.

TABLE 1

Operating conditions	Parameter: Pulsed current	Parameter: Steady current
Temperature of bar, ° C	600	600
Average voltage, volts	3	0.9
Average amperage, amps	1,200	400
Time, hours	100	100

TABLE 2.—ANALYTICAL RESULTS, CERIUM BAR; IMPURITY ELEMENT CONTENT, WEIGHT PERCENT

Impurity	Pulsed current	Steady current
Molybdenum:		
Initial	0.23	0.23
Cathode end	.78	.19
Anode end	.13	.21
Copper:		
Initial	.47	.45
Cathode end	1.6	1.1
Anode end	.07	.31
Oxygen:		
Initial	.016	.011
Anode end	.028	.010
Cathode end	.009	.010
Iron:		
Initial	.013	.013
Anode end	.185	.150
Cathode end	.005	.001
Manganese:		
Initial	.07	.09
Anode end	.10	.16
Cathode end	.01	.06

TABLE 3.—ANALYTICAL RESULTS, LANTHANUM BAR

Impurity	Pulsed current	Steady current
Copper:		
Initial	0.46	0.27
Anode end	.08	.13
Cathode end	5.0	.66
Carbon:		
Initial	.84	.84
Anode end	1.1	.77
Cathode end	.51	.76
Iron:		
Initial	.31	.10
Anode end	.38	.11
Cathode end	.037	.08
Molybdenum:		
Initial	.15	.086
Anode end	.099	.072
Cathode end	.30	.095

What is claimed is:

1. A method for purification of a reactive metal comprising passing a pulsed direct current through an impure specimen to cause migration of the impurities by electrotransport, and removing said impurities.

2. The method of claim 1 in which the reactive metal is a rare earth metal.

3. The method of claim 2 in which the metal is cerium.

4. The method of claim 2 in which the metal is lanthanum.

5. The method of claim 1 in which the impure reactive metal is in the form of a rod having a length of at least about 6 inches and a diameter of at least about ½ inch.

6. The method of claim 1 in which the temperature of the metal is maintained at about 600° C.

7. The method of claim 1 in which the average voltage of the pulsed field is about 3 volts and the average amperage of the resulting current is about 1200 amperes.

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