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ELECTROLYTIC PROCESS FOR PRODUCING ALLOYS OF LITHIUM

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Fig. 1.

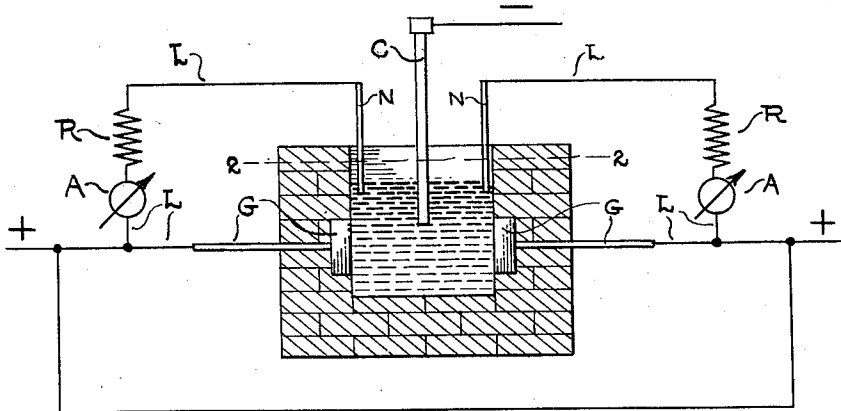
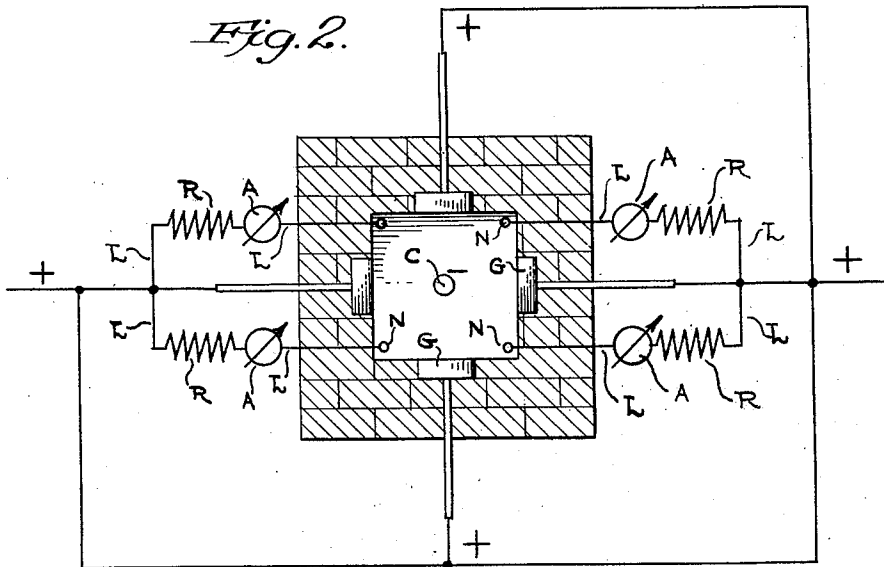


Fig. 2.



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ELECTROLYTIC PROCESS FOR PRODUCING ALLOYS OF LITHIUM

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The present invention relates to an electrolytic process for producing alloys of lithium and more particularly to the electrolytic process of producing alloys of lithium and a metal fusing at a high temperature, particularly a heavy metal.

It is well known, that the properties of certain metals may be influenced by the addition of metallic lithium to molten baths of said metals. The addition of lithium to molten baths of metals such as nickel, iron, etc., or alloys thereof, has been found to be objectionable for various reasons. For instance, metallic lithium floats on the surface of the molten metal because of its low specific gravity and burns or vaporizes on the surface of the bath because of its low boiling point and of its easy combustibility. All of the aforesaid objectionable reactions occur before the lithium has had an opportunity of reacting, or alloying with the metal or alloy in the molten bath which is undergoing treatment. It has been impractical consequently to introduce more than a few tenths of one per cent of metallic lithium into molten baths of metals or alloys, particularly those having higher melting points. Even the addition of relatively small quantities of metallic lithium to molten metal baths involves considerable loss of the relatively expensive metallic lithium. For the aforesaid reasons, as well as others, it has been unsatisfactory and impractical to utilize metallic lithium on a commercial and industrial scale.

The present invention contemplates a method of producing lithium in the form of alloys which can be used on a practical and an industrial scale without being subjected to the disadvantages noted hereinabove.

It is another object of the invention to provide an electrolytic process of producing alloys of lithium and a metal, especially a heavy metal, in a practical, satisfactory, economical and commercial manner.

It is a further object of the invention to provide an electrolytic process for producing alloys of lithium and a metal, especially a heavy metal, in such a manner that the lithium and other metal is deposited simultaneously at the cathode.

The invention also contemplates providing an electrolytic process of producing an alloy of lithium and a metal in such a manner that the proportion of lithium to the other metal which is deposited at the cathode may be controlled and regulated.

Other objects and advantages of the invention will become apparent from the following description.

Broadly stated, the invention contemplates utilizing plates, sheets, bars, rods, or the like of the metal to be deposited and alloyed with lithium, and arranging said plates, sheets, bars, rods or the like in such a relation to a graphite anode or anodes that when current is passed through a fused electrolytic bath, an alloy of lithium and the metal is deposited at the cathode, preferably in the form of an alloy having a certain percentage of lithium and a certain percentage of the other metal.

For the purpose of facilitating an understanding of the invention by those skilled in the art, the following specific illustrative example is given. It is to be noted, however, that the specific example is merely illustrative and the invention is not to be limited thereby.

The following description is taken in conjunction with the accompanying drawing in which:—

Fig. 1 represents a sectional elevational view, somewhat diagrammatic, of an electrolytic cell in which my invention may be carried out; and

Fig. 2 illustrates a sectional view, somewhat diagrammatic, taken on the line 2—2 of Fig. 1.

For the purpose of producing an alloy of

lithium and nickel, for instance, an anode is made of graphite plates and nickel rods N. The graphite plates G are arranged in the form of a square or rectangular or other cross section with the nickel rods at the corners of such figures. The nickel rods are in an electrical connection via lines L containing a resistance R and ammeter A with the graphite anode or anodes. By regulating the area of the graphite plates to the area of the nickel rods, and the resistance R used in a connection between the nickel rods and the graphite plates, it is possible to control and regulate the amount of current passing from the graphite anodes and the nickel anodes to the cathode, as one skilled in the art will readily understand. For instance, if 2500 amperes were being passed through the anode the nickel rods and graphite plates could be arranged so that 150 amperes would pass through the nickel or metal rods and the other 2350 amperes would pass through the graphite plates. The 150 amperes would effect the deposition of a certain amount of metal whereas the 2350 amperes would effect the deposition of a certain amount of lithium. By calculating the amount of lithium and the other metal deposited by the aforesaid currents, it is possible to determine the composition of the lithium alloy to be deposited at the cathode C.

In carrying the present invention into practice, it is preferable to use an electrolytic cell, such as illustrated in Figs. 1 and 2, having a hollow anode preferably in the form of a square shell, the sides of which are graphite plates and the corners of which are nickel rods connected in parallel with the graphite plates. A resistance may be incorporated in the connection between a nickel rod and an adjacent graphite plate in order to further control the amount of current passing through and from the nickel rods and through and from the graphite plates. A cathode, such as a nickel rod may be located in the center of the hollow square anode. Into the cell a molten electrolyte may be poured and then a suitable electric current may be turned on to cause the deposition of a lithium alloy. Usually a halide of lithium or a mixture of halides may be employed as the electrolyte. Potassium chloride, or other appropriate salts, may be added to such an electrolyte for the purpose of facilitating the electrolysis and the deposition of the lithium alloy, or for other purposes. Of course, it is possible to use compounds other than halides, provided such compounds are capable of being transformed into halides or into compounds suitable for the electrolytic deposition of the lithium and the other metals when the current is passed through the electrolytic cell containing such compounds in a fused state. For example, oxides, hydroxides, carbonates and the like may be added to the electrolytic

bath because the chlorine electrolytically evolved at the anode will transform such oxides, etc. into chlorides. In some instances, it may be advantageous to add such oxides, etc., or mixtures thereof to the fused electrolytic bath in the form of briquettes.

In some cases, it is preferable to add a mixture of the lithium electrolyte, say lithium chloride and potassium chloride, with enough of a compound, say the chloride of the other metal or metals to be deposited simultaneously with the lithium at the cathode. By adjusting the composition of the bath, an alloy of lithium of the desired composition may be electro-deposited, as one skilled in the art will readily understand. When the electro-deposition of the alloy commences, the metal or metals to be deposited with lithium will go into solution from the metal rods connected in parallel with the graphite plates. In this manner, if all of the operating conditions are correctly selected, alloys of the desired composition may be obtained even from the very beginning of the electrolysis. The ratio of the surfaces or areas of the graphite plates and the metal rods in the anode have to be adjusted so that the proper amount of lithium and the said metal or metals can be plated simultaneously at the cathode. By controlling or regulating the graphite and metal areas of the anode and/or the resistance in the parallel connection between the graphite plates and the metal rods, it is possible to cause the deposition of lithium alloys of a desired or selected composition.

Lithium alloys of certain metals when deposited at the cathode in a manner set forth hereinabove, rise to the surface of the fused or molten bath, when the lithium content of such an alloy is relatively high. In these cases, the lithium alloy can be skimmed off the surface of the bath like pure lithium by means of suitable utensils, such as ladles or the like. In other cases, particularly alloys having low lithium content, the alloy deposited has a relatively high specific gravity and is more or less soft. The deposited alloy sticks to the surface of the cathode from which it can be easily scraped off by means of suitable tools. As a general rule, in order to prevent contamination of the alloy by foreign metals, it will in general be advisable to select the cathode of a metal which is a component of the lithium alloy to be electro-deposited. Thus, for example, it is advantageous to employ a nickel cathode when producing a lithium-nickel alloy. In case a lithium-iron alloy is to be produced, then a low carbon steel cathode is employed. In this manner, a relatively pure alloy of lithium can be deposited at the cathode. Of course, when the deposited lithium alloy is skimmed off the molten electrolyte, or is removed from the

cathode in a spongy condition, a portion of the electrolyte may be contained in the alloy. In these cases, as one skilled in the art will readily understand, the lithium alloy may be purified in any well known manner, such as by remelting under a salt or equivalent cover.

It will be appreciated that in accordance with the present invention, it is possible to produce alloys of lithium with heavy metals having a content of lithium which exceeds by far the lithium content in old industrial alloys containing lithium. These old alloys contained only a few tenths of one per cent of lithium. With the production of lithium alloys, it is possible to produce pre-alloys which are rich in lithium and which preferably contain more than 3% thereof. Such alloys with a high lithium content may be used advantageously in industry.

The present invention may be carried into practice in a variety of ways, but the following specific example is given so that one skilled in the art can carry the present invention readily and quickly into practice.

An electrolytic cell is provided with a hollow anode of a square or rectangular cross section. The anode is constructed so that the sides consist of graphite plates and the corners consist of nickel rods. The cathode may consist of a nickel rod. The electrolyte preferably consists of a melted mixture of lithium chloride and potassium chloride. The anode and cathode may have any suitable size but I prefer to use nickel rods which are about 10 to about 25 millimeters in thickness. The nickel rods may be connected in parallel with the graphite plate in any suitable manner as long as they do not form an arc with parts of the graphite plates. In other words, in a cell having a hollow square anode, for example, the graphite portions of said anode do not cover each side entirely and the metal rods can be installed in the corners of the anode without any interference of current lines emanating from the anode.

By passing a suitable electric current, say about 1550 amperes and 1480 amperes through the graphite and nickel anodes, respectively, or say about 1550 amperes and 600 amperes through the graphite and metal anodes, respectively, alloys of different percentages are deposited at the cathode. The nickel alloy thus obtained contains about 20% or about 40%, respectively, of lithium. It is also possible of course to obtain an alloy with a higher as well as a lower lithium content. The alloy may rise to the surface of the electrolyte or it may stick to the cathode in a spongy or granular form. The deposited lithium-nickel alloy may be removed in any appropriate manner as mentioned hereinabove. By remelting the deposited alloy at a temperature of about 400°

C. to about 500° C. in an iron crucible and if necessary under a salt cover preferably in vacuum, the lithium composition may be purified of contaminating electrolyte.

Although I have mentioned certain specific metals and other substances, it will be observed that my invention may be carried into practice by utilizing any other appropriate and equivalent metals and substances. For instance, instead of nickel, cobalt, manganese, gold, platinum, silver, copper, iron and the like may be employed. A metal of the foregoing type shall be designated in the specification and claims as "a metal melting at a relatively high temperature above about 600° C." As to further variations of the invention it is to be observed that the present process contemplates the production of alloys the components of which have decomposition voltages which are quite far apart in the electromotive series such as lithium or the like and nickel or the like. These components are deposited simultaneously at the cathode in selected proportions by passing an electric current through a nickel anode or the like and a graphite anode of a cell containing a bath in which a compound containing lithium or the like (i. e. a metal more electronegative than nickel or the like). By regulating the electric current passing through the nickel anode and the graphite anode to such amounts that the equivalent of the anions deposited at the graphite anode correspond to the equivalent of the more electronegative metal (lithium) deposited at the cathode while the equivalent of the anions deposited at the nickel (less electronegative metal) anode correspond to the equivalent of nickel (or other less electronegative metal) deposited simultaneously with lithium (or other more electronegative metal) at the cathode. It is obvious that selected or pre-determined proportions of lithium (or other more electronegative metal) and of nickel (or other less electronegative metal) may be simultaneously deposited at the cathode by regulating the electric current in the foregoing manner.

The terminology used herein (electronegative etc.) is in accordance with modern practice. For instance, such practice and terminology is described in textbooks, such as Blum and Hogaboom's "Principles of Electroplating" (published by McGraw-Hill Company, New York).

I claim:

1. The process of producing a lithium alloy containing a metal melting at a relatively high temperature above about 600° C., which comprises establishing an electrolytic cell having a fused bath containing a lithium compound capable of permitting the electro-deposition of lithium and maintaining a cathode and a plurality of anodes including a graphite anode and an anode of a metal

to be electro-deposited, and passing an electric current through said cell via said graphite anode and said metal anode to cause the deposition of an alloy of lithium and the said metal at the cathode

2. The process of producing a lithium alloy containing a metal melting at a relatively high temperature above about 600° C., such as set forth in claim 1, in which the lithium and the metal are deposited simultaneously in the form of an alloy at the cathode.

3. The process of producing a lithium alloy containing a metal melting at a relatively high temperature above about 600° C., such as set forth in claim 1, in which the areas of the graphite and metal portions of the anode are so selected that the ratio of the amount of lithium and the amount of other metal to be deposited at the cathode can be controlled

4. The process of producing a lithium alloy containing a metal melting at a relatively high temperature above about 600° C., such as set forth in claim 1, in which substances or mixtures thereof containing a metal or metals to be deposited with lithium are added to the fused electrolyte.

5. The process of producing a lithium alloy containing a metal melting at a relatively high temperature above about 600° C., such as set forth in claim 1, in which a substance containing the metals to be deposited with lithium are added to the electrolyte in such a condition as to be capable of being transformed into compounds capable of permitting the metals to be electro-deposited therefrom.

6. The process of producing a lithium alloy containing a metal melting at a relatively high temperature above about 600° C., such as set forth in claim 1, in which a compound of lithium or a metal to be produced is added to the fused electrolyte before or during electrolysis and is of such a constitution as to be capable of being converted into a chloride by the action of chlorine liberated at the anode.

7. The process of producing an alloy, such as a lithium alloy, by the electrodeposition of a more electronegative metal (lithium) and a less electronegative metal (nickel) at the cathode of an electrolytic cell which comprises establishing a fused electrolytic bath containing a compound of a more electronegative metal (lithium) and a plurality of anodes including a graphite anode and an anode of a less electronegative metal (nickel), passing an electric current through said cell, and regulating the current passing through said graphite anode and metal anode to such amounts that the equivalent of the anions deposited at the graphite anode correspond to the equivalent of the more electronegative metal (lithium) de-

posited at the cathode while the equivalent of the anions deposited at the metal anode correspond to the equivalent of the less electronegative metal (nickel) deposited at the cathode whereby an alloy having selected proportions of the more electronegative metal (lithium) and of the less electronegative metal (nickel) is electro-deposited at the cathode.

In testimony whereof I have hereunto set my hand.

HANS OSBORG.