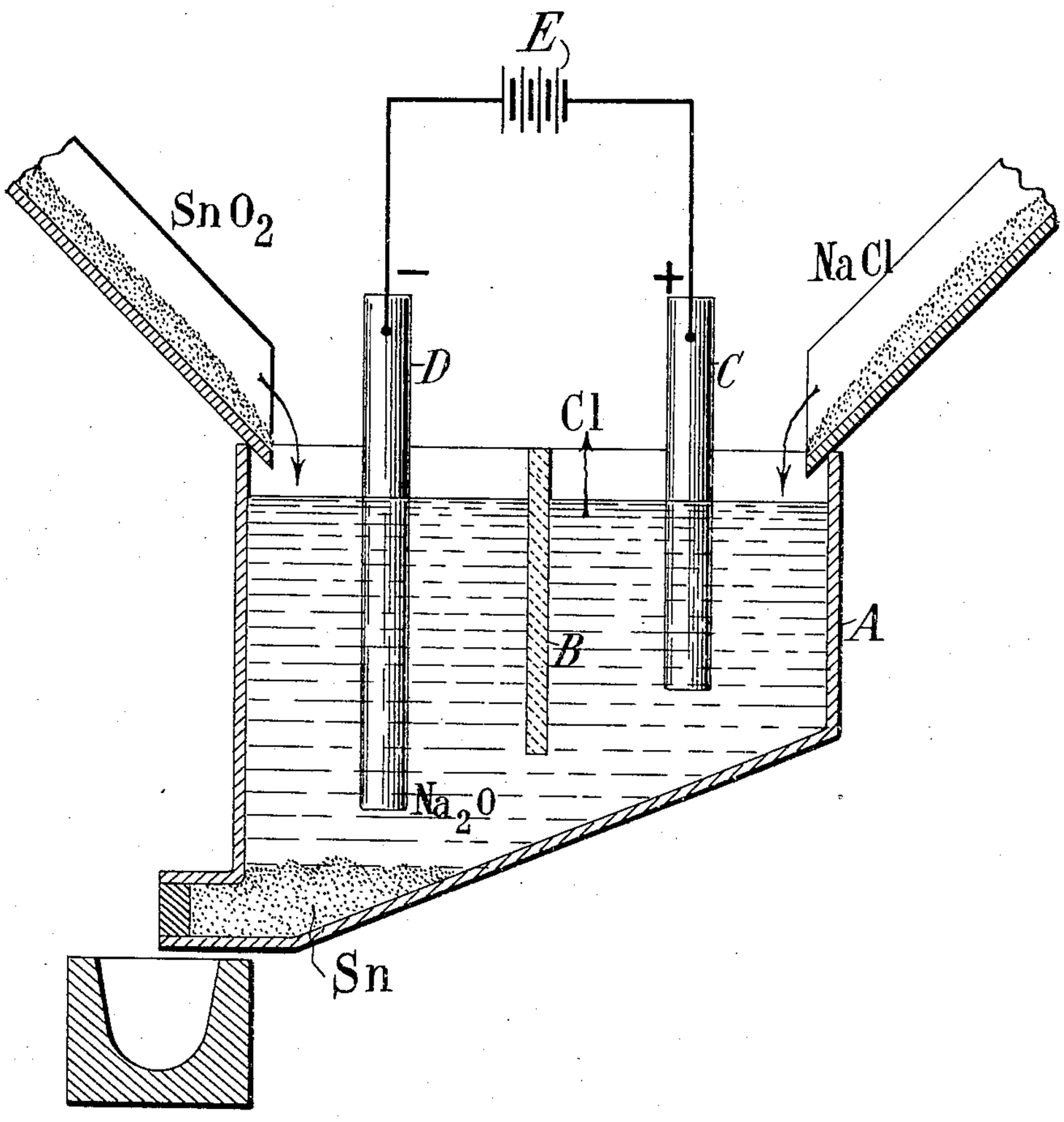
No. 771,646. PATENTED OCT. 4. 1904.

F. VON KÜGELGEN & H. DANNEEL.

PROCESS OF OBTAINING METALS.

APPLICATION FILED JULY 29, 1903.

NO MODEL.



WITNESSES:

Fred Whitz

René Muine

INVENTORS:

Heinrich Danneel and Franz Von Kugelgen,

By Attorneys,

Arthur C. Fraser & Co

No. 771,646. Patented October 4, 1904.

UNITED STATES PATENT OFFICE.

FRANZ VON KÜGELGEN, OF HOLCOMBS ROCK, VIRGINIA, AND HEINRICH DANNEEL, OF BRESLAU, GERMANY, ASSIGNORS TO THE WILLSON ALUMINUM COMPANY, OF NEW YORK, N. Y., A CORPORATION OF NEW YORK.

PROCESS OF OBTAINING METALS.

SPECIFICATION forming part of Letters Patent No. 771,646, dated October 4, 1904.

Application filed July 29, 1903. Serial No. 167,415. (No specimens.)

To all whom it may concern:

Be it known that we, FRANZ VON KÜGELGEN, residing at Holcombs Rock, in the county of Bedford and State of Virginia, and HEINRICH DANNEEL, residing at Breslau, Germany, both subjects of the German Emperor, have invented certain new and useful Improvements in Processes of Obtaining Metals, of which the following is a specification.

Our invention relates to an electrolytic process for the obtaining of metals from their oxids or for the obtaining of alloys of various metals and for the obtaining at the same time an alkali oxid and a halogen.

Alkali hydroxids are at present generally obtained by the electrolyzing of aqueous solutions of alkali salts. There are some processes, however, which depend on the electrolyzing of a fused alkali salt and the consequent separation of the metal at the cathode, after which it is converted into an oxid or a hydroxid. Such a process involves a great consumption of electrical energy on account of the high voltage required for the separation of the alkali metal from its salt. By the use of a suitable depolarizer, such as oxygen, the voltage required for separation of the alkali can be reduced. There are a number of metals which are ordinarily reduced from their ores with carbon, which process involves various difficulties and disadvantages. Such metals, for example, are tin, aluminium, &c. According to our invention we propose to introduce the oxygen in the form of an oxid of such a metal at or adjacent to the cathode of a cell, so as to depolarize the products passing to the cathode in the same manner as free oxygen, though in a less degree. There will then be formed at the cathode (with an electrolyte consisting of an alkali salt) not the alkali, but the oxid thereof, and the metal which was before combined with oxygen in the form of an oxid is reduced and obtained as a pure metal. As an example, we will describe the obtaining of tin from tin oxid, which at present is generally accomplished by reduction with carbon and with great difficulties and disadvantages. In our process there is the additional advantage of simultaneously obtaining chlorin and sodium oxid from the sodium chlorid.

In any suitable cell sodium chlorid (fused either beforehand or by the current) is electrolyzed in the presence of tin oxid. The sodium from the chlorid separates at the cathode and reduces the tin oxid, the chlorin of the chlorid passing off at the anode. The following equation represents the operation, approximately:

$$SnO_2+4NaCl=Sn+2Cl_2+2Na_2O.$$

We may induce the formation of metallic sodium at the cathode by using a low supply of oxygen or a high voltage, when there will be formed a tin sodium alloy, of which the reducing power can be utilized in the making of metallic tin and solutions of alkalies. The metallic tin goes to the bottom, and the sodium oxid sinks and covers the tin as a molten layer adjacent to the cathode. Any suitable means can be used for withdrawing these products from the chamber. For example, they may be tapped off together, the tin filling the bottom of the tapping-pot and the sodium oxid in a layer above it, so that they can be easily separated. The sodium oxid withdrawn may contain some salt, from which it can be separated by fractional solution, transforming the oxid into a hydroxid.

The process can be similarly employed for obtaining other metals from their oxids or for obtaining alloys from the oxids of two or more metals—as, for example, aluminium and copper or tin and copper. The chlorin developed at the anode can be used in the manufacture of chlorid of lime and for other purposes. Any other haloid than the chlorid may be employed—as, for example, an iodid or a bromid—the chlorid, however, being more generally and cheaply available.

The most important advantages of the process are that it obtains at one operation three commercial products—namely, the metal or alloy, the alkali oxid, and the halogen. The metal is obtained free from carbon. The efficiency of the process—that is, the ratio of

the actual output to the theoretical—is very high. The energy consumed is comparatively little, the voltage required being low and corresponding to the voltage of decomposition of a chlorid of the metal to be obtained. For example, in the reduction of tin oxid as above explained the voltage required is that which would be necessary to decompose tin chlorid. We have not determined exactly the minimum voltage which will be effective; but it is lower than that needed (about 4.2 volts) for the decomposition of sodium chlorid.

The process may be carried out with very cheap materials.

The process may be carried out with a great variety of apparatus. In this apparatus the materials may be added in continuous streams or may be added from time to time in considerable quantities. In either of these cases the process is regarded as continuous in the sense that the composition of the electrolyte is maintained substantially the same as in the beginning, and the reactions referred to are occurring with substantial continuity. We have illustrated diagrammatically in the accompanying drawing the manner of carrying out the process with a specific form of apparatus, although it is understood that the particular type of apparatus used is not essential to the process.

A is an electrolytic cell divided into an anode and a cathode chamber by means of a porous diaphragm B. This diaphragm is not essential except to prevent the alkali oxid from going to the anode. The anode C is preferably of carbon and the cathode D of iron, these being connected, as usual, with any source of current, (indicated at E.) A bath of fused sodium chlorid is provided in the cell, and tin oxid is introduced into the cathode-chamber. At the cathode sodium is liberated and combines with the oxygen of the tin oxid. The reduced tin falls to the bottom of the cell and is removed as desired. Chlorin is liberated at the cathode and may be collected in any suitable manner. The sodium oxid is withdrawn from the cathode-chamber and additional sodium chlorid added in the anode-chamber, so as to continue the reactions referred to. The operations are substantially the same with other alkaline haloids and metallic oxids than those specifically referred to.

Though we have described with great particularity of detail certain processes embodying our invention, yet it is to be understood that the invention is not limited to the specific processes disclosed. Various modifications thereof in the several steps and in the order thereof and in the ingredients used may be made by those skilled in the art without departure from the invention.

What we claim is—

1. The process which consists in electrolyzing a haloid of an alkali in the presence of an oxid of a metal, thus obtaining the metal, an oxid of the alkali, and the halogen, and maintaining a supply of the haloid and the oxid by adding fresh quantities thereof as they are decomposed.

2. The process which consists in introducing a metallic oxid into the cathode-chamber of an electrolytic cell the electrolyte of which is composed of a haloid of an alkali, thus obtaining the metal, an oxid of the alkali, and the halogen, withdrawing alkali oxid from the cathode-chamber, and maintaining the electrolyte by adding the haloid in the anode-chamber.

3. The process of obtaining a metal, an oxid of an alkali, and a halogen, which consists in electrolyzing the corresponding haloid of the alkali in the presence of an oxid of the metal, whereby the haloid is decomposed to liberate the halogen and the alkali reduces the metal oxid, forming the oxid of the alkali and freeing the metal, the operation being continued by maintaining a supply of the haloid and the metallic oxid and withdrawing the alkali oxid.

4. The process of obtaining metallic tin, sodium oxid and chlorin, which consists in electrolyzing sodium chlorid in the presence of tin oxid whereby the sodium chlorid is decomposed to liberate chlorin and the sodium reduces the tin oxid forming sodium oxid and freeing tin, the operation being continued by maintaining a supply of the sodium chlorid and the tin oxid and withdrawing the sodium oxid.

In witness whereof I, FRANZ VON KÜGELGEN, have hereunto signed my name in the presence of two subscribing witnesses.

FRANZ VON KÜGELGEN.

Witnesses:

GEO. F. SEWARD,

J. TURNER MOREHEAD.

In witness whereof I, HEINRICH DANNEEL, have hereunto signed my name in the presence of two subscribing witnesses.

HEINRICH DANNEEL.

Witnesses:

JOUST KATZ,

RICHARD ABEGG.