

No. 765,001.

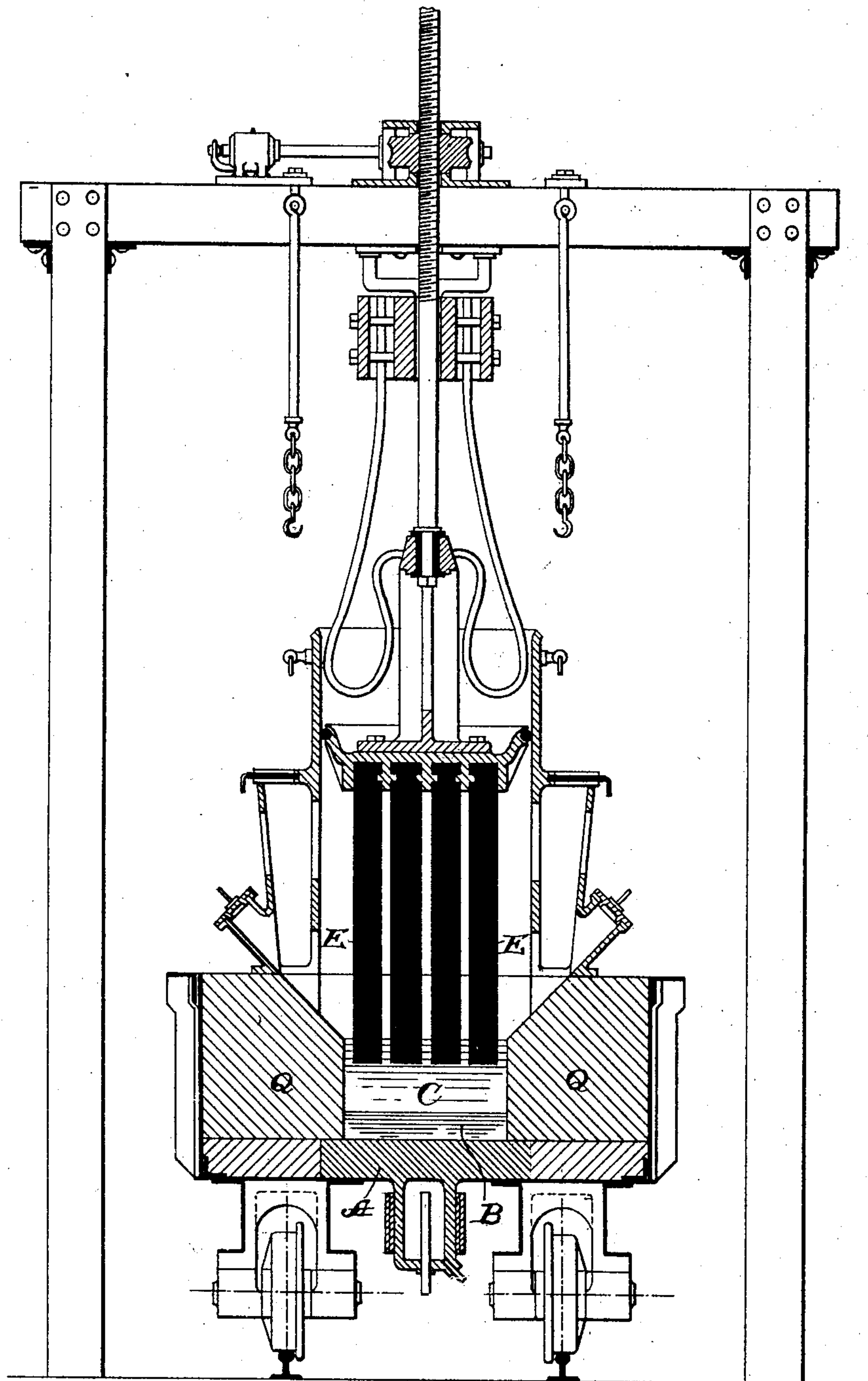
PATENTED JULY 12, 1904.

G. GIN.

PROCESS OF MANUFACTURING VANADIUM AND ITS ALLOYS.

APPLICATION FILED MAY 9, 1903.

NO MODEL.



Witnesses.

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UNITED STATES PATENT OFFICE.

GUSTAVE GIN, OF PARIS, FRANCE.

PROCESS OF MANUFACTURING VANADIUM AND ITS ALLOYS.

SPECIFICATION forming part of Letters Patent No. 765,001, dated July 12, 1904.

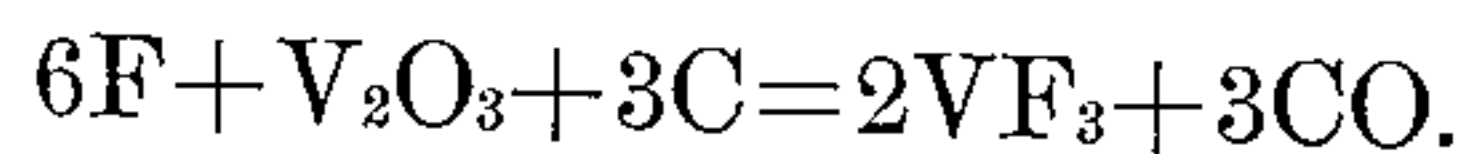
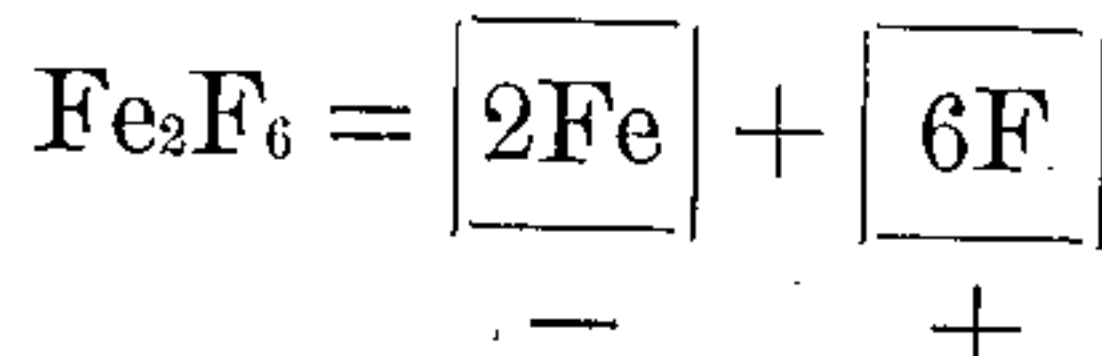
Application filed May 9, 1903. Serial No. 156,426. (No specimens.)

To all whom it may concern:

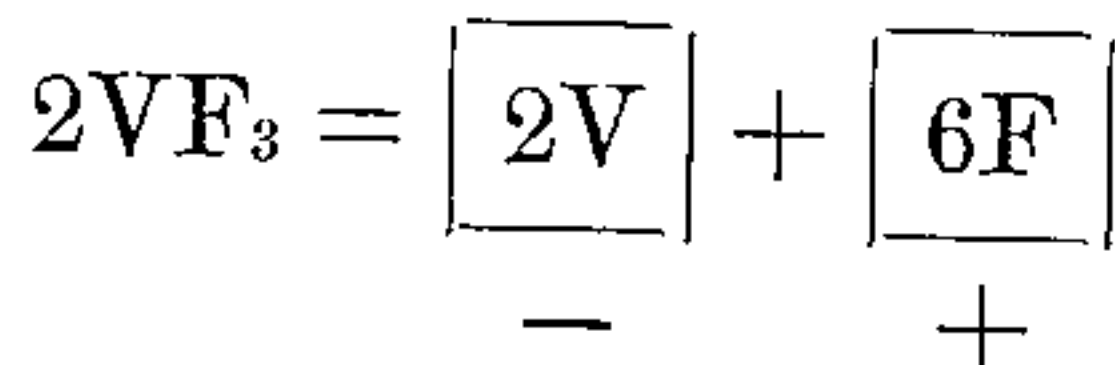
Be it known that I, GUSTAVE GIN, a citizen of the French Republic, and a resident of Paris, France, have invented a certain new Process for the Manufacture of Vanadium and Its Alloys, of which the following is a specification.

The object of my process is the manufacture of vanadium and of its alloys by the electrolytic method.

The principle of my process rests upon the great conductivity of the trioxid of vanadium and upon the facility with which the trifluorid of vanadium is obtained by treating the trioxid with fluorin in presence of carbon. In order to show how these characteristic properties can be utilized to produce ferro-vanadium, for instance, let it be supposed that sesquifluorid of iron dissolved in melted fluorid of calcium be electrolyzed by using an anode formed by an intimately-agglomerated mixture of trioxid of vanadium and of carbon, the cathode being constituted by a bath of metallic iron. The ferric fluorid being decomposed by the current, the fluorin freed at the contact of the anode attacks the trioxid of vanadium, which yields its oxygen to the carbon, while trifluorid of vanadium is formed according to the following reactions:



The fluorid of vanadium formed enters into solution in the fluorid of calcium and in its turn is electrolyzed.



The vanadium set free combines with the metallic iron at the cathode, and the fluorin set free at the anode forms a fresh quantity of fluorid of vanadium, as shown above, which is electrolyzed anew, so that the ferric fluorid mentioned above only serves to prime the

operation and to furnish the fluorin, serving as a means of transport to cause the vanadium to pass from the anode to the cathode.

It is evident that my process is applicable under similar conditions to the industrial manufacture of alloys of vanadium with other metals, such as copper, aluminium, manganese, &c. It will be sufficient to replace the cathodic bath of iron by a bath of the metal which must come in the alloy.

Having set forth the principle of my invention, I will now proceed to explain how I act in practice.

The trioxid of vanadium prepared by the known process, consisting in calcining the vanadic acid in presence of carbon, is mixed with a suitable proportion of finely-powdered retort-coke or petroleum-coke. Then an addition of hot tar is made in a quantity sufficient to obtain by malaxating a homogeneous and plastic paste. After being malaxated in a special kneading-trough outwardly heated the paste passes into a mill, wherein it is crushed by very heavy steel rollers. The paste on leaving the mill is pounded under stamps and then forced by hydraulic pressure into a draw-plate apparatus similar to those used for the manufacture of carbon electrodes. Finally, prismatic or cylindrical blocks are obtained, which are baked, safe from contact with the air, in furnaces of a high temperature. The electrodes thus manufactured until required for use are kept beneath a layer of a dry pulverulent material, so as to thoroughly protect them from contact with the air. It is evident that the electrodes can be manufactured by the direct agglomeration of vanadic acid or of tetroxid of vanadium, which passes at a high temperature and in the presence of carbon to the state of trioxid; but owing to the elimination of oxygen and of carbon resulting from the use of superior oxids porous products are obtained less dense and the electric resisting power whereof is more considerable.

In order that the operation may be better understood, I annex to this specification a drawing of an electrical furnace (shown in sec-

tion) which may be used in carrying out my process, although I do not claim any of the features shown in said drawing.

There is a multiple anode E and a water-cooled metallic cathode A. The lining of the crucible Q is such that it cannot be attacked by the ingredients of the bath. During the operation the bottom of the crucible is filled with a molten bath B of the metal with which the vanadium is to be alloyed, if an alloy is desired. The upper portion of the crucible is filled with a bath C, calcium fluorid in fusion. When the apparatus is ready to work, the fluorid of vanadium or the fluorid of the metal with which the vanadium is to be alloyed is introduced in the calcium-fluorid bath and the operation takes place according to the reactions mentioned above. For alloys having more than twenty-five per cent. of vanadium the cathodic section should be appreciably less than the active surface of the anodes. A good result and a sufficiently liquid bath are obtained with a medium density of two amperes per square centimeter of active surface of the anodes and of six amperes per square centimeter of section of the cathode, the voltage being between eleven and twelve volts. As I said at the beginning, the ferric fluorid introduced into the bath at the commencement of the operation only serves to set going the dissolution of the anode and the electrolysis of the vanadium. However, as there is a loss of a certain quantity of fluorin transformed into

gaseous tetrafluorid of carbon upon contact with the carbon in excess in the mixture forming the anode it is desirable to compensate that loss by adding to the bath from time to time a certain proportion of ferric fluorid. The iron constituting the cathodic bath is introduced in a metallic state and in small quantities at a time after each tapping of ferrovanadium. If no iron be introduced in the bath, almost pure vanadium may be obtained, which is very difficult to tap in a liquid state and must be extracted from the furnace in a solid state.

Having now fully described my said invention, what I claim, and desire to secure by Letters Patent, is—

The process for the electrical manufacture of vanadium alloys which consists in subjecting an anode made of an agglomerated mixture of carbon and vanadium oxid to electrolytic action in a fused bath consisting of calcium fluorid and a fluorid of the metal with which the metal is to be alloyed, introducing the metal with which the vanadium is to be alloyed, in a metallic state in proximity of the cathode, and tapping the resultant alloy product.

In testimony whereof I have hereunto set my hand in presence of two witnesses.

GUSTAVE GIN.

Witnesses:

ADOLPHE STURM,
J. ALLISON BOWEN.