UNITED STATES PATENT OFFICE.

PIERRE MANHES, OF LYONS, FRANCE, ASSIGNOR OF ONE-HALF TO THE SOCIÉTÉ ANONYME DE MÉTALLURGIE DU CUIVRE, PROCÉDÉS PRE. MANHES, OF SAME PLACE.

PROCESS OF MANUFACTURING NICKEL AND COBALT.

SPECIFICATION forming part of Letters Patent No. 574,068, dated December 29, 1896.

Application filed April 23, 1894. Serial No. 508,701. (No specimens.) Patented in France December 9, 1893, No. 234,750; in Germany January 21, 1894, No. 77,427, and in England April 6, 1894, No. 6,914.

To all whom it may concern:

Be it known that I, PIERRE MANHES, metallurgical engineer, a citizen of the Republic of France, residing at 3 Rue Sala, Lyons, in the Republic of France, have invented certain new and useful Improvements Relating to the Manufacture of Nickel and Cobalt, (for which I have obtained Letters Patent as follows: in France, No. 234,750, dated December 9, 1893; in Germany, No. 77,427, dated January 21, 1894, and in Great Britain, No. 6,914, dated April 6, 1894,) of which the following is a specification.

My invention relates to the manufacture of nickel and cobalt.

For the purpose of producing nickel and cobalt the ores of these metals are nearly always treated by fusion for matte. Sulfurous ores bear the sulfur necessary for the formation of the matte, while non-sulfurous ores are supplied with sulfureted materials or sulfur in the first fusion of these ores. The matte produced is then either successively roasted and fused, or preferably treated in the converter by the Manhes process. Whatever method may be employed the iron may be easily enough and completely enough eliminated, but it is not the same with the sulfur. The product obtained is always a sulfid of nickel or a crude nickel containing a comparatively large proportion of sulfur, the ulterior treatment of which has heretofore necessitated long, difficult, and costly operations, producing only a metal of very imperfect quality. According to my said invention I treat this sulfid of nickel or crude nickel for obtaining by a simple, rapid, and economic method ingots of nickel similar to those of the other usual metals, and adapted for the uses of the various industries which require commercially-pure nickel. It will therefore be understood that my process has for its starting-point the treatment of sulfid of nickel or of crude nickel previously almost altogether freed from iron by one of the processes hereinbefore mentioned or by any other process.

For the sake of simplicity I shall hereinafter mention only nickel, it being quite understood that the whole process may likewise be applied to cobalt in order to obtain the latter in a metallic state.

In the course of long and numerous experiments I have found that the sulfur contained in crude nickel freed from iron can be completely eliminated by the simple fusion of this metal in mixture and in contact with certain basic or alkaline reagents or fluxes mixed with chlorids of the same nature. These reagents are lime, baryta, magnesia, soda, potash, or other similar substances from the chemical point of view, to which chlorids of calcium, lime, barium, magnesium, sodium, potassium or the like are added, the chlorid of calcium being the body usually designated by this name, having the chemical formula CaCl, and the chlorid of lime being the commercial chlorid of commerce containing hypochlorite, the formula of which is CaO,ClO. A portion of the sulfur is eliminated in the state of sulfurous acid, while the other portion combines with reagents added for forming a scoria, which is almost exclusively a basic or alkaline sulfid, according to the nature of the reagents employed.

Although use may be made of the various reagents before enumerated or of other similar reagents, I usually employ in practice a mixture of lime and chlorid of calcium, or, better still, commercial chlorid of lime, (CaO,ClO,) as these materials are preferable from an economic point of view and give, moreover, excellent results.

Having thus explained the nature of my invention and the principles upon which it is based, I will now summarily describe a metallurgical operation, taking as an example the treatment of a crude nickel produced by the working of matte in the converter by a first fusion, the matte containing very little iron, but inclosing still a more or less large proportion of sulfur.

The fusion with the special reagents hereinbefore mentioned may be effected in any suitable apparatus, in the metallurgical furnace, on the sole or in the crucible on condition that the apparatus or furnace in question can easily produce and maintain the high temperature necessary for the fusion of the pure

nickel. In practice I preferably operate upon the sole and in a reverberatory furnace heated by gas, such as the Siemens furnace or other similar furnace, provided that it shall be able to fulfil the desired conditions as regards the temperature.

I must here observe that whatever apparatus or furnace may be used it must be provided in the interior with a neutral or basic lining, not in view of any reaction to be obtained in the metallurgical operation, but because the nature of the reagents employed renders the use of acid walls or linings impossible.

The furnace being suitably heated, I commence by providing the surface of the sole with a sufficiently thick layer of the mixture of lime and chlorid of lime, so as to form a kind of false sole, the object of which will hereinafter be explained. Then I introduce into the furnace the crude nickel granulated or crushed to pieces after having been mixed with a sufficient quantity of the same reagents. Next I close the door of the furnace and heat slowly, the temperature being gradually raised until the fusion of the materials introduced into the furnace is complete. During this fusion the crude metal in contact with the reagents gives up to the latter the greatest part of the sulfur which it contains, while another part is eliminated in the state of sulfurous acid. By reason of its density the molten nickel gradually separates from the scoria formed and reaches the bottom of the furnace. There it encounters the false sole made of lime and chlorid of lime, traverses it slowly, and while transforming it into scoriæ gives up to the same the little sulfur which it may still have retained. When the fusion of the materials is complete, there remains upon the sole of the furnace commercially-pure metallic nickel, upon which is a scoria formed almost exclusively of sulfid of calcium. When the operation has reached this point, the scoria is first caused to flow out and then the nickel, which on leaving the furnace is passed into molds adapted for the various uses to which the metal may be put.

If the operation has been well conducted and the temperature has been sufficient, all the materials at the moment of the casting must be in a state of perfect fluidity. The scoria contains only insignificant traces of nickel, which, however, is not lost, for this scoria is melted again with the ore in the furnace wherein the first fusion or preliminary melting of the ore takes place. It constitutes, in fact, a doubly-valuable flux by reason of the lime and the sulfur which it contains. When employing this scoria, an important saving is achieved by the lime in the fusion of silicated or silicious ores and by the sulfur in the fusion of non-sulfurous ores, to which a sulfurizing element which is almost always very costly must be added.

Although in the foregoing description I have described my improved process with especial reference to the desulfurizing of nickel sulfid from which the iron has been previously almost wholly eliminated, it will be understood that in some cases the same process may be effectively employed in desulfurizing nickel ores from which the iron has not been eliminated—such, for instance, as nickel fonte—that is to say, the metal obtained by the fusion and reduction of oxidized ores or nickel, for example, the well-known ores of New Caledonia, which are an alloy in variable proportions of carbureted iron and nickel and which always contains a little sulfur, generally two or three per cent.

Where nickel is employed in the metallurgy of iron and steel, it may often be advisable to use nickel fonte without previously separating the iron and nickel, and I have found in actual practice that in carrying out the described process with an ore of this character it is possible to obtain complete desulfuration of the metal without a sensible loss of either iron or nickel.

It is almost impossible to represent by chemical formula the reactions which take place in this process, for that would presuppose precise proportions of the reagents employed, and such is not the case. In fact, these proportions vary according to the nature and the composition of the material treated. As an example applicable to the treatment of the material for the elimination of iron, the action may be represented: $Ni_2S+FeS+O_3=FeO+SO_2+Ni_2S$. One has thus as the product a subsulfuret of nickel, (Ni_2S,) the sulfur of which may be eliminated as follows, (formula as an example only:) $4Ni_2S+CaO+CaCl+O=2CaS+SO_2+SCl+Ni_8$.

The formulæ given above are mere examples, as in actual operation the workman who conducts it adds the reagents in small quantities. He follows up the operation by taking samples, and stops the operation when the purification of the metal has reached the desired point.

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

1. The herein-described process of producing pure commercial nickel, said process consisting in first, forming in the operating-furnace a false sole or bottom of an alkaline or basic reagent mixed with a chlorid of the same base; second, mixing the granulated nickel with a quantity of reagents of the same base as those forming the false sole or bottom and placing said nickel and reagents on the false sole or bottom; and finally, heating the mixture to a fusing-point to permit the separation of the sulfur, a portion of the latter being driven off as sulfurous acid, and the remainder combining with the mixed reagent and with the reagent of which the false sole or bottom is formed as the fused nickel sinks by gravity through the false sole or bottom, substantially as specified.

2. The herein-described process of produc-

ing pure commercial nickel, said process consisting in first forming in the operating-furnace a false sole or bottom of mixed lime and chlorid of lime; second, mixing the crushed or granulated ore or nickel with lime and chlorid of lime and heating the mass until the fused metal is separated and sinks by gravity through the reagent to the bottom of the furnace, the contained sulfur being partly driven off as sulfurous acid and the remaining sulfur being combined with the lime to form an alkaline or basic sulfid, substantially as specified.

In witness whereof I have hereunto set my hand this 4th day of April, 1894.

PIERRE MANHES.

Witnesses:
XAVIER JANICOT,
JEAN GERMAIN.