UNITED STATES PATENT OFFICE.

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PROCESS OF MANUFACTURING MANGANESE AND ALLOYS OF MANGANESE FREE FROM CARBON.

SPECIFICATION forming part of Letters Patent No. 489,303, dated January 3, 1893.

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To all whom it may concern:

Be it known that we, WILLIAM H. GREENE and WILLIAM H. WAHL, both citizens of the United States, and residents of Philadelphia, Pennsylvania, have invented a Process of Manufacturing Manganese and Alloys of Manganese Free from Carbon, of which the following is a specification.

The object of our invention is to manufacture on a commercial scale, manganese and manganese alloys which will be wholly free from carbon.

The industrial application of manganese in the operations of steel making, and recently in the manufacture of the alloys known as manganese steel, manganese bronze, and other metallic mixtures in which this metal enters as an essential constituent, has made it desirable to produce metallic manganese on a commercial scale in a state of the highest possible purity, and cheaply enough to permit of its use in these operations. Hitherto, manufacturers, for the want of the pure metal, have been compelled to employ the alloys of manganese and iron made in the blast furnace and known as spiegeleisen and ferro-manganese, these alloys containing from six to eighty-five per cent. of manganese with five or six per cent. of carbon, and small quantities of silicon, phosphorus and other impurities. The most persistent efforts heretofore made to produce, cheaply enough for industrial purposes, a manganese practically free from carbon and iron have failed.

The processes heretofore employed or proposed for the production of manganese may be placed in two groups:—In one, an oxide of the metal (either in the form of the sesquioxide, or the di-oxide) or the carbonate is intimately incorporated with finely divided carbon, and subjected to an intense heat in crucibles, whereby the reduction is effected. As a result of many experiments conducted on this plan of reduction, we have satisfied ourselves that it is impossible to produce a metal free from carbon. The manganese we have produced by numerous modifications of this general plan invariably contained about six per cent. of combined carbon, even when the quantity of carbon employed was insufficient to effect a complete reduction of the oxides, nor could this carbon be eliminated from the metal by fusing it, in presence of sundry fluxes, with more oxides. These results confirm those of other experimenters. In another group, may be placed those processes in which the chloride or fluoride of manganese is reduced by subjecting it, under various circumstances, to the action of sodium. By methods of this class manganese may be obtained chemically pure but they have proved far too costly to be used commercially. The electrolytic method of reduction has been experimentally attempted on a small scale, but the impossibility of using a carbonaceous anode in this operation because of the certainty of forming a carbonide of the metal is one of the several difficulties which the electro-metallurgist has not been able to overcome. Alloys of copper containing varying proportions of manganese have indeed been made successfully on a commercial scale by the electric furnace method, but the necessity of using electrodes of carbon in this method renders the production of the pure metal impossible.

We will now proceed to describe our invention of a process for producing metallic manganese entirely free from carbon, and containing only such slight quantities of iron and other impurities, such as silicon, phosphorus, &c., as are within the permissible limit in the manufacture of metals on a large scale, where the term commercially pure is used to designate the product.

In the operation of our process, the manganese ore composed substantially of manganese di-oxide, and contaminated with more or less iron, is finely ground and digested with sulphuric acid, (specific gravity 1.84) diluted with two or three times its volume of water. The iron passes into solution, while the oxides of manganese are only slightly affected. We have found that the above named proportions of dilution for the acid should be adhered to in order to obtain the most satisfactory results, since, if a more concentrated acid solution be used, the manganese oxide will be powerfully attacked and dissolved, while, if a more dilute acid be employed, the time consumed in the removal of the iron will be unduly prolonged. The operation is facilitated by constant agitation of the mixture so as to expose fresh portions of the ore to the action of the acid. When the removal of the iron is accomplished, the liquor is drawn off and the purified ore is washed with water to remove all traces of the acid, and dried. If the operation has been conducted properly, the percentage of iron in the ore is thereby reduced to a few tenths of one per cent. The acid liquid may be treated by well known methods for the recovery of the waste in the form of copperas. In operating with a commercially pure ore, or where the presence of iron in the metal is not objectionable, this preliminary purification, will, of course, not be necessary. The ore is now to be reduced to the condition of a lower oxide, preferably to that of manganese monoxide, by any convenient method. The reduction to manganese monoxide presents several important practical advantages. Manganese monoxide, being the lowest known oxide of manganese, will demand less of the reducing substance to subsequently remove its oxygen, and this oxide is better adapted for such subsequent reduction by reason of being fusible at a much lower temperature than the other oxides of the metal.

For the reduction of the manganese di-oxide to a lower oxide, we have found the following method to answer satisfactorily. The commercially pure native ore, or the commercially purified ore is introduced into an oven having preferably the form of a horizontal cylinder, and mounted so as to permit of being rotated about a horizontal axis. The oven is provided with suitable openings for the admission and exit of gases. In an oven answering to this general description, the ore is heated to redness in a current of reducing gas, for which purpose we may employ petroleum-vapor, hydro-carbon gases, carbon monoxide, or water gas. By this operation, di-oxide and sesqui-oxide (corresponding respectively to the chemical formulæ MnO_2, Mn_2O_3) are converted first to the protosesquioxide (Mn_3O_4) and then to the gray oxide or monoxide of the composition MnO.

The final step of our process consists in reducing the manganese protosesquioxide or manganese monoxide to the metallic state. We accomplish this by heating it in contact with a metal capable of removing and appropriating its oxygen and setting free the manganese. The presence of a flux facilitates the re-action and the gathering into a single mass of the resulting metal, which, when no flux is used in the operation, is found disseminated through the mixture in the form of globules or shot, which require to be separated, collected, and remelted. In this operation we use a crucible or chamber formed of, or lined with, a material free from carbon, and preferably also free from silica.

For certain uses for which the metal may be found suitable, the presence of silicon in small quantity, say to the amount of three per cent., is not detrimental, and for metal of this quality, the reduction of the manganese protosesquioxide or monoxide may be performed in silicious crucibles.

We have found the following mode of operation to yield the best results. Manganese monoxide is introduced into a crucible or chamber lined with lime or magnesia or other material free from carbon and silica and capable of resisting the action of the flux, metallic aluminum is added in the proportion required to effect the reduction of the manganese monoxide present, (that is to say in the proportion of fifty-five parts of aluminum to two hundred and thirteen parts of manganese monoxide) and there is also added a quantity of some suitable flux. This may consist either of fluorides such as fluor-spar or cryolite or mixtures of both, or, in case the operation be conducted in silicious vessels of silicates of potassium, sodium, calcium, aluminium, and magnesium in various proportions. The mixture is then heated to the temperature at which the re-action takes place. If desired, however, the manganese monoxide intimately incorporated with a convenient quantity of the flux, may be introduced into the reducing chamber or crucible, together with the aluminum in the proportions above named, and the mixture then heated to the temperature at which the reaction takes place. If instead of monoxide, the protosesquioxide is under treatment the proportion of oxygen-appropriating metal should be correspondingly increased, in accordance with the change in chemical equivalents involved. When the presence in the metal, of silicon in small proportion is not objectionable, the reduction may easily and effectively be accomplished by either of the foregoing procedures, by the use of a readily fusible silicious flux, such for example as powdered glass, and the reduction may be effected in silicious crucibles.

To avoid the contamination of the resulting metal with aluminum, we have found it preferable to add in the reducing operation, somewhat less aluminum than would be required to reduce the manganese oxide completely. By careful observance of this precaution the quantity of aluminum remaining in the product will be inappreciable.

By the several operations above described, there results metallic manganese entirely free from carbon and containing only such small quantities of iron, silicon, and other impurities, that, for commercial purposes, it may be considered to be pure. A product of such high grade of purity has not yet, to our knowledge, been made on a commercial scale, and we are enabled by our process to manufacture it at a lower cost than has heretofore been possible. The resulting metal exhibits the property of being quite stable in the air, an evidence of its freedom from carbon, while all the so-called manganese reduced in contact with carbon, after exposure to the air for a few days only, disintegrates and falls to powder. The residuum containing the aluminum oxide may be treated if found desirable, to regenerate the aluminum.

If, instead of pure manganese, an alloy of manganese is desired, the metal which it is wished to alloy with the manganese may be introduced either with the aluminum, which is used as the reducing agent, or with the ore, as in the herein described case where a ferruginous manganese ore is employed in the manufacture of a ferromanganese entirely free from carbon.

Having now described our process, we claim as our invention and desire to secure by Letters Patent:—

1. In the art of producing metallic manganese, or manganese alloys free from carbon, the herein described process which consists in reducing the ore to the condition of a lower oxide, and then reducing such lower oxide to the metallic state by heating it, in a reducing chamber free from carbon, in contact with substantially the chemically equivalent quantity of a metal capable of removing its oxygen, substantially as described.

2. In the art of producing metallic manganese, or manganese alloys free from carbon, the herein described process which consists in reducing the ore to the condition of a lower oxide, and then reducing said lower oxide to the metallic state by heating it, in a reducing chamber free from carbon and silica, in contact with substantially the chemical equivalent quantity of a metal capable of reducing its oxygen, substantially as described.

3. In the art of producing metallic manganese, or manganese alloys free from carbon, the herein described process which consists in digesting the manganese ore with diluted sulphuric acid, then reducing the purified ore to the condition of a lower oxide, and then reducing such lower oxide to the metallic state by heating, in a reducing chamber free from carbon, in contact with substantially the chemically equivalent quantity of a metal capable of removing its oxygen, substantially as described.

4. In the art of producing metallic manganese, or manganese alloys free from carbon, the herein described process which consists in digesting the manganese ore with diluted sulphuric acid, then reducing the purified ore to the condition of a lower oxide and then reducing such lower oxide to the metallic state by heating it, in a reducing chamber free from carbon and silica, in contact with substantially the chemically equivalent quantity of a metal capable of removing its oxygen, substantially as described.

5. In the art of producing metallic manganese or manganese alloys free from carbon, the herein described process which consists in reducing the ore to manganese monoxide, then reducing said monoxide to the metallic state by heating it in contact with substantially the chemically equivalent quantity of a metal capable of removing its oxygen, substantially as set forth.

In testimony whereof we have signed our names to this specification in the presence of two subscribing witnesses.

WILLIAM H. GREENE.
WILLIAM H. WAHL.

Witnesses:
HENRY HOWSON,
HARRY SMITH.