

UNITED STATES PATENT OFFICE.

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PROCESS OF PRODUCING METALLIC ALLOYS.

SPECIFICATION forming part of Letters Patent No. 490,961, dated January 31, 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 Producing Metallic Alloys, of which the following is a specification.

The object of our invention is to provide a cheap and efficient means for the production of certain metallic alloys, and our process consists substantially in utilizing metallic silicides, for the reduction of certain difficultly reducible oxides, or of such as cannot be reduced by means of carbon without the introduction of an objectionable quantity of carbon into the resulting metal.

The term metallic silicides as we use it, is intended to include all metallic compounds or mixtures in which the element silicon is present in such quantity as to justify their designation as siliciferous alloys, or siliconized alloys, terms which are well understood by metallurgists. It is not practicable in this definition to name a minimum quantity of silicon that would suit all cases, for the reason that silicon affects the physical properties of different metals differently, and what would be a small proportion for one metal would be a large proportion for another, and because the presence of other elements may profoundly alter the properties of the alloy. Thus, in commercial cast iron the proportion of silicon may vary from a trace to about 3.5 per cent. as a maximum. Ordinary cast iron containing 3.5 per cent. of silicon we would therefore not consider to be a silicide, but if an iron containing 3.5 per cent. silicon at the same time contain a proportion of carbon, not exceeding one per cent., we would consider it for our purposes to be a silicide. Other metals than iron we consider to be silicides when they contain two per cent. of silicon. When such silicides are heated with metallic oxides in presence of a suitable base, such as lime, magnesia or alumina, the oxygen of the oxide combines with the silicon forming silica which at once unites with the base forming a fusible silicate that separates as slag, while the metals set free then combine together forming an alloy. By suitable regulation of the proportions and character of the silicide, metallic oxide and flux; or, by repeating the opera-

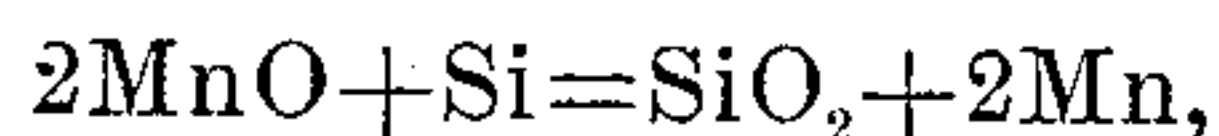
tion of fusion with fresh additions of ore, or by the addition of any given metal to the original charge or to the product of the first re-action, we are enabled to produce metallic alloys or mixtures having any required composition.

Our process, it will be observed, enables us to effect the reduction of numerous metallic oxides without the aid of carbon, a circumstance which in certain cases especially in the manufacture of metals used in the production of certain special steels, is of vital importance. In fact, we wish to affirm in general terms that we effect the reduction of metallic oxides under entirely new conditions which enable us to produce with advantage not only well known and useful metallic alloys and compositions, but also others heretofore unknown having new and valuable properties. As an example we will cite the case of manganese steel. By the present method of manufacturing this alloy, which consists in the addition of ordinary ferro-manganese to fluid iron, the proportion of manganese that can usefully be introduced into the product is limited by the carbon which to the amount of five to six per cent., is present in the ferro-manganese, and which cannot be eliminated therefrom because of its affinity for manganese. By our process, we are able to produce an alloy of iron and manganese containing so small a proportion of carbon as to permit of the introduction of a much larger proportion of manganese into steel than by the present method, without introducing so much carbon as to overstep the permissible limit. It is evident that in all our operations, whether performed on the hearth of a furnace, or in crucibles, the presence in either, or in the flux, of free carbon, must strictly be avoided.

We will now describe our process in detail, taking as an example its application to the manufacture of manganese steel. In this case we employ the commercial products known under the names of ferro-silicon, silico-spiegel, and silico-ferro-manganese, which may be described as silicides of iron or of iron and manganese containing a variable proportion of silicon, usually from six to thirty per cent., and a comparatively low percentage of carbon.

Since, for reasons previously stated, in the absence of carbon in notable proportion is of great importance in manganese steel, we employ for our purpose a silicide containing as high a proportion of silicon and as low a proportion of carbon as possible. Silicon irons and spiegels containing as much as fifteen or twenty per cent. of silicon, and with carbon not exceeding one per cent., can readily be obtained, and by special selection of ores and fluxes can be made even richer than this in silicon. As a rule, also, the quantity of carbon present in such silicides varies with the silicon in an inverse ratio, carbon decreasing as silicon increases and vice versa. A silicide, which may be either ferro-silicon or silico-spiegel of suitable composition having been selected, it is melted on the hearth of a furnace having preferably a lime or magnesia lining, and when melted a quantity of the non-oxide or protoxyde of manganese (preferably the former) with which there has previously been incorporated a quantity of any suitable flux, is added thereto. The reaction takes place promptly, the silicon of the ferro-silicon seizes upon the oxygen of the manganese ore, and is thereby converted into silicic oxide which forms with the flux a liquid slag, while the manganese set free by the reduction of the ore combines with the molten iron set free from the silicide. Agitation of the charge will, of course, facilitate the operation by bringing more quickly the ingredients of the charge into intimate contact. The whole charge of manganese ore and flux may be added to the ferro-silicon at once, or the addition may be made by portions until a sufficient quantity of the oxide has been employed to utilize the reducing power of all of the silicon that was present in the ferro-silicon, thus reducing a chemically equivalent quantity of manganese oxide to the metallic state.

Assuming that we operate with a silicide containing iron, eighty-eight per cent., silicon, ten per cent.; carbon, one per cent.; as the reaction will take place according to the equation



we employ silicide and manganese oxide in quantities that satisfy the above proportions, i. e. for every twenty-eight parts of silicon in the silicide, one hundred and forty-two parts of manganese monoxide are added, and the quantity of lime, magnesia, or alumina or a mixture of these, that will completely combine with the silica to form a fusible silicate.

We have found it necessary to use a larger quantity of manganese ore than that required by theory, for the reason that a certain quantity of the manganese oxide is always seized upon by the silica and passes into the slag in the form of manganese silicate. We have found the following proportions by weight of charge to yield good results:—ferro-silicon containing ten per cent. silicon one per cent.

carbon one hundred pounds. Manganese monoxide, seventy pounds. Lime, fifty pounds. A charge of this composition will yield about one hundred and twenty-eight pounds of a metallic alloy having this composition: iron seventy per cent., manganese twenty-nine per cent., carbon 0.7 per cent. silicon trace.

Assuming that the permissible percentage of carbon in a certain manganese steel is 0.5 per cent., then one hundred pounds of a manganese alloy of the above composition will produce by mixture with forty pounds of decarburized iron, one hundred and forty pounds of manganese steel of the composition iron 78.8 manganese 20.7 carbon 0.5 silicon trace.

In the preparation of a manganese steel containing the same percentage of carbon by melting decarburized iron with ordinary ferro-manganese containing eighty per cent. manganese and 5.5 per cent. carbon, the resulting metal would contain 92.23 per cent. iron and only 7.27 per cent. manganese. Or, making the comparison on the basis of equivalent quantities of manganese, the manganese steel made from the ordinary ferro-manganese would contain for 20.7 per cent. manganese 1.4 per cent. carbon: that made by our process would contain for 7.27 per cent. manganese only 0.18 per cent. carbon.

By strictly analogous methods of operation, other special steels or alloys of iron may be formed, thus the substitution of tungstic oxide for the manganese oxide in the previously described operation will result in the formation of an alloy of iron and tungsten applicable to the manufacture of tungsten steel.

In many cases, it is obvious that a metal of the desired composition may be obtained directly by one operation on the furnace hearth. Thus for the production of a manganese steel of a given composition the required proportions of scrap wrought iron and ferro-silicon of a suitable composition may be melted on the hearth, in contact with the manganese oxide.

In the manner described, alloys of copper with difficult reducible metals may be obtained by fusing appropriate oxides with copper silicide, and other silicides will doubtless be found useful for similar purposes.

We are aware that in the manufacture of steel by what is commonly known as the open hearth process, pig iron and scrap, containing a small and varying proportion of silicon, are melted in contact with oxides of iron, and that the chemical reaction which takes place in this operation is similar to that which occurs in the operation of our process. The carbon and silicon of the iron, both of which, but essentially the first, it is the object of the open hearth steel process to remove, are burned out by the oxygen of the iron ores. But with the similarity of the chemical reactions the analogy between our process and the open hearth steel process ceases.

In the open hearth, the process is essentially

one of decarburization, and the separation of the small quantity of silicon from the pig iron of the charge, is merely an incident. The presence of silicon in the pig irons employed in this operation is wholly unnecessary, and in the choice of such pig irons those which contain but little silicon are preferred, and its total absence does not in the least affect the operation of the process.

In the open hearth process the silicon of the cast iron is an accidental and objectionable constituent which it is desirable to remove. On the contrary, for our purpose the silicon is absolutely essential, and the higher its percentage the more efficient does our process become.

We are also aware that in the commercial reduction, remelting, and casting of many metals and alloys it is difficult or impossible to prevent the retention or the formation of small quantities of oxide, and the absorption of certain gases, such as carbonic oxide and atmospheric oxygen by the metals, and that the presence of even very minute quantities of such oxide and occluded gases has a very unfavorable influence on the strength, ductibility, and other desirable qualities of the metal, and renders it extremely troublesome to roll or obtain castings free from blow-holes.

These difficulties are due to the fact that the presence of slight quantities of oxides and occluded gases prevents the intimate coalescence of the particles of the metal and the production of a perfectly homogeneous texture.

And we are aware that it has long been the practice to counteract the deleterious influences above named by subjecting the metal prior to its withdrawal from the furnace, or cupola, or crucible, or in the ladle just before pouring into the mold, to a species of purification or refining in which the objectionable traces of oxides or harmful occluded gases are removed by the addition to the reduced or remelted metal or alloy while in the molten state of minute quantities of some powerful deoxidizing agent.

For the purpose of such purification or refining, phosphorus, manganese, aluminum, magnesium, and silicon are more or less commonly used, sometimes in the form of compounds or alloys, and sometimes in the elementary form.

As examples, we cite the addition of phosphorus in small quantity, generally in the form of phosphor-copper, or phosphor-tin to copper, brass and bronze, to burn out the traces of cuprous oxide and make a stronger and tougher metal or alloy;

the addition of minute quantities of metallic magnesium to metallic nickel to remove occluded carbonic oxide; of small quantities of ferro-manganese, or ferro-silicon, to molten steel in the open hearth process at the close of the melting, and of copper, tin, and zinc silicides to metallic copper, tin, and zinc, for the same general purpose,

to insure the production of homogeneous metal and sound castings. These operations,

though depending on the general principle of chemical reduction are not comparable with our invention which differs radically in the object attained, in the mode of procedure, and in the scope of its application. The silicides, in the cases above referred to, are added to metals previously reduced by agents other than silicon, and are used in a finishing operation for the purpose of removing small and generally minute quantities of certain objectionable impurities unavoidably contracted in the previous operation of reduction by carbon, or in the remelting, and if they are added in quantities greater than may be required for the purification of the metals, this is done for the purpose of forming a silicon alloy, which is foreign to the purpose of our invention.

Our process relates exclusively to the reduction of oxidized ores of metals by bringing such oxides in proper proportion in contact with metallic silicides, and effecting the reduction of the ores solely by the silicon of the silicides with the aid of heat. This metallurgical operation which we have devised, differs substantially and radically from the above described operation of purification of metals contaminated with small quantities of oxide or by occluded gases acquired in the process of their reduction by carbon, or in the remelting; and, we accordingly disclaim such uses of metallic silicides as being foreign to the purpose of our invention.

We claim as our invention:—

1. In the art of manufacturing metallic alloys, the herein described process which consists in heating to a suitable temperature and in presence of suitable fluxes a metallic oxide, in contact with a silicide of a metal capable of alloying with the reduced metal whereby the primary reduction of the metallic oxide to the metallic state is effected by the silicon of the silicide employed and the reduced metal alloys with the base of the silicide.

2. In the art of manufacturing metallic alloys, the herein described process which consists in heating to a suitable temperature in a furnace chamber or crucible free from carbon and in presence of suitable fluxes, a metallic oxide in contact with a silicide of a metal capable of alloying with the reduced metal whereby the primary reduction of the metallic oxide to the metallic state is effected by the silicon of the silicide employed and the reduced metal alloys with the base of the silicide.

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.