

UNITED STATES PATENT OFFICE.

PAUL GIROD, OF UGINES, FRANCE.

MANUFACTURE OF STEEL.

1,043,090.

Specification of Letters Patent.

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No Drawing.

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To all whom it may concern:

Be it known that I, PAUL GIROD, a citizen of the Republic of Switzerland, residing at Ugines, Savoy, France, have invented certain new and useful Improvements in the Manufacture of Steel; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

The present invention relates to the de-oxidation of iron or steel, hereinafter designated by the term "steel," which has been previously melted and partially de-carburized, and, if possible, even de-phosphorized, in a furnace of any kind, such as an acid-lined or basic-lined Bessemer or Thomas furnace, open hearth furnace, or other de-carburizing or oxidizing furnace.

Prior to my present invention it has been proposed to de-oxidize in an electric furnace a metal which has been previously oxidized in a preparatory furnace, by cobling the steel, and then reheating it in the electric furnace under a slag containing reducing bodies, particularly calcium carbide. In these instances, however, the preliminary oxidation of the metal has been carried as far as possible, *i. e.*, to a point where it retains but very small quantities of carbon, silicon and manganese and it is assumed that in the cooling operation the oxid of iron contained in the metal is separated out. The characteristic defect in this former practice is that on account of the low proportion, amounting in some cases to almost an entire absence of not only carbon but silicon and manganese in the cooling metal there is no reaction within the metal sufficient to drive out the iron oxid to the extent required for the results contemplated by my present invention. In contrast to this former practice, I interrupt the oxidation in the furnace used for the preliminary treatment of the steel, in order that there may be left in the body of the metal entering the electric furnace, a sufficient quantity of carbon, silicon and manganese to effect the reactions which I have found necessary for the practically complete elimination of the oxides present, and in order that the products of the reaction, proceeding within the body of the metal shall not be a mere iron oxid difficult to fuse, but chiefly triple silicates of manganese, iron and silicon forming a readily fusible slag.

In carrying out my invention in the Thomas or Bessemer furnace, instead of over-blowing the metal, I interrupt the blowing before the complete elimination of the carbon, silicon and manganese. As a result, the oxidation of the iron itself is diminished and consequently the amount of oxides which have to be subsequently eliminated. Furthermore, there is a corresponding diminution in the amount of occluded gases, particularly of hydrogen which, resulting from the decomposition of the watery vapor contained in large proportion in the air blown in, is always present in the metal.

In determining the length of the blow and consequently the volume of air admitted and its oxidizing effects, I contemplate leaving in the metal at the termination of the blow sufficient quantities of carbon, silicon and manganese to effect the elimination of the iron-oxid by reaction within the mass resulting, as hereinbefore indicated, in the production of a slag consisting chiefly of triple silicates of manganese, iron and silicon. It is therefore characteristic of the invention that the reactions within the electric furnace resulting in the elimination of the iron-oxides take place within the metal itself, whereas in the previous practice, the attempt to eliminate the oxides has been due wholly to surface action between the oxides rising to the top of the bath and the superincumbent slag. Instead, therefore, as in the former practice, of the oxides being held back in large part by the metal as it becomes more and more pasty on cooling, so that the gaseous products alone make their way through the pasty mass, the highly fusible silicates due to the reactions incident to the practice of my invention are formed and in part separate, the carbon monoxid or carbon di-oxid, hydrogen, and nitrogen escaping in great measure through the pasty or partially solidified metal. As the temperature lowers, there finally comes a time at which the metal becomes so pasty that no more of the silicates of manganese and of iron can escape and they remain temporarily occluded in the metal together with some portion of the gases. Finally, the temperature of the furnace is raised to melt the charge, and a slag (preferably neutral) is thrown upon the surface of the metal. This slag may conveniently contain CaO, silica, and, in some cases a flux, such as

fluor spar, (calcium fluorid), and varies according to circumstances and particularly according to the furnace lining. The throwing in of the slag referred to precedes the raising of the temperature of the furnace for the reheating of the metal and the slag must be of sufficient thickness so that the metal will be protected from the oxidizing gases which may be present even though the electric furnace is fairly well closed.

As soon as the metal has a tendency to become liquid, the gases retained at a lower temperature, make their escape and as soon as the metal is completely liquid the slags within the metal, which slags now consist exclusively of silicates of manganese and of iron rise to the surface where they become incorporated with the surface layer of slag. When the preliminary oxidizing operation is carried on, for instance, in a basic-lined or Thomas converter, for example, a test piece taken from the metal should show practically the following composition, to wit: carbon, about 0.10% to 0.15%, silicon, about 0.1% to 0.2%. This last amount being practically difficult to obtain, it might be realized by adding ferro-silicon with quite a low or high percentage of silicon, the addition being made either before or after the blow in the Thomas furnace or in the Bessemer furnace, or even later, as in the ladle, or in the electric furnace itself. The test piece should also show manganese about 0.2% to 0.3% and it likewise would contain an amount of phosphorus, varying according to the purity of the cast iron used, and which may be from 0.025% to 0.030% if the cast iron was nearly free of phosphorus, or which may attain 0.050% to 0.100% if the metal was impure. In the latter case, the oxidation should take place in the Bessemer furnace, because the oxidation in the electric furnace would be more expensive.

The metal being of the composition above specified, is transferred to the electric furnace either directly or by means of a ladle of some suitable kind, the transfer being made at a temperature of about 1500° C. to 1600° C. In this condition, the metal could not be tapped without additions, inasmuch as the proportion of the oxids or protoxids therein contained may still amount to 0.5% to 0.8%, or even higher. After its introduction into the electric furnace, a convenient quantity of scrap or the like, of nearly the same composition or of greater purity is added, either in the form of cold scrap, turnings, clippings, forge scale or mill scale, or of the same material, in a hot state, coming directly from the forge or from the rolling mills, so that the temperature will be lowered from 1500° C. or 1600° C. down to 1250° C. or 1300° C.

It is preferable, for the production of the

best results, that the lowering of the temperature be effected rapidly, instead of slowly and progressively; and, in order to save time, the scrap, turnings, and the like, may be previously placed in the electric furnace and the metal may be run in from them; so that they not only serve to lower the temperature of the metal as desired, but the heat units thus expended are utilized in melting the scrap and adding it to the volume of the furnace charge. When the temperature is thus lowered, a considerable evolution of gases takes place resulting from the reaction of the carbon upon the occluded oxids, and large black spots appear on the surface of the bath which consists of liquid or semi-liquid cinders formed by the action of the manganese and of the silicon upon the oxids retained in the metal. The evolution of the gases is at first accompanied with an ebullition of the metal which lessens progressively as the temperature decreases. When the temperature has fallen to from 1200° C. to 1250° C. on the surface of the bath, neither the gases nor the slags can thereafter escape from the metal; a swelling up of the surface of the metal is then noticeable. At this stage, if the proportion of carbon, silicon and manganese contained in the metal has been sufficient, the occluded oxids have been reduced by the carbon, manganese and silicon, and transformed into silicates of iron and manganese. If, on the contrary, the proportion of carbon, silicon and manganese was not sufficient to effect the reduction of the oxids contained in the metal, the operation can be repeated one or several times, taking the precaution, however, after having reheated the metal in the presence of a suitable slag, to make further additions of silicon, carbon and manganese before cooling it again.

As soon as the bath has become sufficiently quiet and the temperature sufficiently low so that the occluded gases, the hydrogen and nitrogen may partially and for the most part escape or separate from the metal, the neutral slag hereinbefore referred to is drawn from the surface of the metal. This being done, the temperature of the electric furnace is again raised. As soon as the metal tends to become liquid again, the gases that were retained at a lower temperature, effect their escape, and as soon as the metal is completely liquid again, the slags contained within the metal, which now consist exclusively of silicates of manganese and of iron in contra-distinction to iron oxid rising to the surface, where they merge with the superficial layer of slag.

According to the degree of refining desired, the metal can then be tapped from the furnace, after the addition of any alloying metals, such as silicon, manganese, chromium, etc., if those metals are desired in the

final composition. Usually, however, for the purpose of insuring the complete de-sulfurization and the more complete elimination of the other impurities which may still remain in the metal, the first slag is removed, by tapping it off or in some other suitable way, and a second slag of the same composition is added; if the furnace lining is silicious, the slag may likewise be silicious, and if the furnace lining is basic, the slag may be basic. After the second slag has become entirely fluid, and the metal has the proper proportion of alloying metal or of carbon, it is finally in condition to be tapped from the furnace and used for the purpose intended. The carburizing of the metal may be effected by any suitable carburizer of appropriate composition, as, for instance, by carbon itself, or by pig iron, or the like.

Under the conditions specified, the period of de-oxidation and of de-gasification, lasts about from ten to twenty minutes, and the final refining operation lasts from 45 minutes to 2 hours, according to the composition and the desired quality of the final product. It may even require a still longer time if the metal is of a complex composition and especially where important additions of alloys and nickel or other metals are to be made before tapping.

Where the cast iron treated is a phosphoric pig, that is, when the pig or the scrap preliminarily melted and treated in the Thomas, Bessemer, or open hearth furnace, or even in the electric furnace, still contains a large amount of phosphorus, it will be advisable to avoid as much as possible the elimination of the phosphorus in the electric furnace before the de-oxidation begins, by super-heating the metal in the Bessemer, open hearth, Thomas, or other furnace for the purpose of eliminating almost the entire contents of carbon silicon and manganese, (and aluminum, if present). It is then necessary, after stopping the blow, to add either in the converter, or in the ladle, or even in the electric furnace where the final reaction is to be made, the carbon, silicon, manganese and eventually aluminum, or one or the other of these bodies only, if they have not been all eliminated. The reducing elements having thus been supplied again to the metal, the latter is charged into the electric furnace and there treated as hereinbefore described.

In some instances, the operator is obliged to melt and treat a very phosphoretic metal in a furnace of the Thomas, open hearth, or other type, or even in an electric furnace, without carrying the de-phosphorization too far. Usually, it is advisable to avoid super-oxidation of the metal by air blowing, on account of the gases that the steel can dissolve. The electric furnace can likewise be charged with very insufficiently de-phos-

phorized steel, but owing to the large amount of phosphorus in such case, it will be necessary to complete the de-phosphorization in the electric furnace by a new oxidation. In this instance, the metal is charged hot, and is not immediately cooled (or at least only to a small extent) in order that the metal may remain in a liquid state. The carbon, silicon, manganese and phosphorus are oxidized preferably by the addition of iron ore, or, in some cases, by blowing air into the metal either through its entire depth or upon its surface only, thereby eliminating the oxidizable elements and especially the phosphorus. After a sufficient oxidation of the elements above referred to, the oxidized slag must be removed and may be replaced by any other appropriate slag (preferably neutral), the effect of which will be, in the first place, to remove the last traces of the phosphoretic oxidizing slag.

When the first or second slag has been removed, as for instance, by tilting the furnace, or in some other approved manner; the carbon, manganese and silicon are added to the metal in order to bring the metal to the desired composition, which is approximately as follows: Carbon .1 to .150, manganese .1 to .2, silicon .1 to .2 or more if necessary. Only after this addition has been made is the cooling of the metal to take place, and this cooling may be permitted to take place naturally, as for instance, by conduction and radiation, or artificially, by the addition of further scrap either cold or more or less hot. The operation is then conducted under the same conditions as those hereinbefore stated.

Referring generally to the practice of the invention and the principles of operation upon which it is based, I may point out that steel of any kind manufactured by the ordinary processes, *i. e.*, by the Bessemer or by the open hearth process, acid or basic, even when containing large quantities of carbon, silicon and manganese, likewise retains iron-oxid which is dissolved in the steel and which cannot be reduced at a high temperature even by means of a very large excess of silicon and manganese. At a low temperature this iron-oxid is, on the contrary, very easily reduced by carbon, silicon and manganese, so that it is not only advantageous not to eliminate completely these materials before transferring the liquid metal to the electric furnace, but, in some cases, it is even advisable to add a further amount of carbon, silicon and manganese before the treatment in the electric furnace, the artificial cooling of the metal in the electric furnace facilitating the reaction of the reducing elements on the oxid which is contained in the metal. Furthermore, in the electric furnace, the oxidation being carried on at a low temperature, the carbon, silicon, manganese and phosphorus contained in the steel

are more easily oxidized than the iron, a circumstance which insures the complete efficiency of the process. Preliminary overblowing being avoided, the expense of such overblowing, requiring, as it does, a prolongation of the operation in the preliminary furnace is wholly absent. It is likewise characteristic of my invention that the escape of the occluded gases is further facilitated, because of the well known fact that the presence of carbon and silicon lowers the capacity of iron or steel to absorb hydrogen. When all of the gases do not succeed in making their way through with the oxids of carbon which may be formed at high pressure, those remaining are occluded in the metal; but when the metal is again heated out of contact with the air, the occluded gases are rapidly eliminated so that there is finally obtained commercially a metal containing but a minimum quantity of gases.

It will, of course, be understood, that the preliminary oxidation of the cast iron may be effected in an electric furnace, if desired, and where it may prove economical or otherwise advantageous to do so.

What I claim is:

1. The method of converting cast iron into steel, which consists in first subjecting the metal to oxidation, interrupting the oxidation before the elimination of the carbon and metallic impurities, and then treating the metal in an electric furnace while carrying sufficient carbon and metallic impurities to react upon the occluded oxids within the metal to produce a slag consisting chiefly of fusible silicates; substantially as described.

2. The method of converting cast iron into steel, which consists in first subjecting the metal to oxidation, interrupting the oxidation before the elimination of the carbon and

metallic impurities, and then treating the metal in an electric furnace while carrying sufficient carbon and metallic impurities to react upon the occluded oxids within the metal to produce a slag consisting chiefly of fusible silicates, any lack of metallic impurities to complete the reaction being first supplied by additions thereof to the partially oxidized metal; substantially as described.

3. The method of converting cast iron into steel, which consists in first subjecting the metal to oxidation, interrupting the oxidation before the elimination of the carbon and metallic impurities, treating the metal in an electric furnace while carrying sufficient carbon and metallic impurities to react upon the occluded oxids within the metal to produce a slag consisting chiefly of fusible silicates, and facilitating the operation by cooling the metal; substantially as described.

4. The method of converting cast iron into steel, which consists in first subjecting the metal to oxidation, interrupting the oxidation before the elimination of the carbon and metallic impurities, treating the metal in an electric furnace while carrying sufficient carbon and metallic impurities to react upon the occluded oxids within the metal to produce a slag consisting chiefly of fusible silicates, facilitating the operation by cooling the metal, and finally raising the temperature to release such portions of the silicates as had been entrapped by the cooling metal; substantially as described.

In testimony whereof I affix my signature, in presence of two witnesses.

PAUL GIROD.

Witnesses:

CAILLAT PIERRE NAPOLEON,
BLACHERE GASTON.