UNITED STATES PATENT OFFICE.

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PROCESS OF TREATING PHOSPHORIC IRON.

SPECIFICATION forming part of Letters Patent No. 590,239, dated September 21, 1897.

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To all whom it may concern:

Be it known that I, AUGUSTE J. ROSSI, a citizen of the United States of America, residing in the city, county, and State of New York, have invented certain new and useful Improvements in Processes of Treating Phosphoric Iron, of which the following is a specification.

It is at present recognized as a metallurgical fact that the phosphoric acid present in many iron ores, and often appearing therein as phosphate of lime or apatite, is in the operation of the blast-furnace reduced to phosphorus, which latter passes almost entirely into the pig metal, leaving, as a rule, but little behind in the slag, and also that whenever the amount of such phosphorus in the iron reaches beyond a few tenths of one per cent., and particularly so when it exceeds one per cent., it so far diminishes the strength of the metal as to render it impracticable for use in the making of castings requiring a certain strength. It is therefore deemed necessary, for instance, in the application of the refining process of the Bessemer acid-converter to avoid the use of pig-iron containing any more than 0.10 per cent. of phosphorus, since this process, as is well understood, does not eliminate the phosphorus and a higher percentage results in steel of inferior tensile strength and resistance.

For the reasons stated ores substantially free from phosphorus are frequently called "Bessemer" ores, and as they are comparatively limited in quantity in certain districts so far as at present known command a relatively higher price than other iron ores in the market. On the other hand, ores containing a very large amount of phosphorus, say as much as two per cent. or over, can be used to produce what is termed "phosphoric" pig, a metal of small value by itself, owing to its weakness, but which, as is well known, may be refined by the so-called "Thomas Gilchrist" or basic process and thus caused to yield an excellent quality of steel. Ores containing a large quantity of phosphoric acid, necessary for the successful operation of the process last referred to, are not, however, always available and may be said to be comparatively rare in the United States. There are, on the other hand, however, in this country a number of ores, quite uniformly and generally distributed, which contain a moderate or intermediate amount of phosphorus, varying, say, from 0.50 per cent. to one per cent., and which are consequently incompetent to produce desirable steel by either the basic or the acid process and yield a pig metal too rich in phosphorus for general use in the foundry, fit only to be employed where little strength is applied, as in stove-castings, for instance. Such ores are therefore at present of small value and are seldom used except in mixture or after concentration, which involves the expense of pulverizing and other preliminary treatment.

Titanic iron ores may be said to be almost invariably Bessemer ores, containing rarely more than a mere trace of phosphorus, and this is particularly the case when these ores are high in titanic acid, containing, say, ten to twenty per cent. thereof, and these titanic ores when smelted yield, as is generally conceded, a pig metal particularly strong and tough, though nearly white, and containing most of the carbon in the combined state.

My invention relates to the redemption of these hitherto substantially useless intermediate phosphoric iron ores, and the object of my invention is to economically treat such ores so as to counteract the effect of the phosphorus in the pig metal smelted from them and increase its strength and toughness. I attain these objects by mixing in proper proportions with such phosphoric ore or phosphoric pig derived therefrom such titaniferous ore—that is to say, such titaniferous ore containing from, say, five per cent. to twenty per cent. or more of titanic acid—whereby the weakening influence of the phosphorus is counteracted or at least so diminished as to render the resultant mixture fit for most foundry purposes. In all cases the proportion of the two ores will be regulated by experience according to the degree of toughness desired in the resultant product and according to the amount of phosphoric acid in the ore as compared with the amount of titanic acid in the ore, and these proportions,

as will be understood by persons skilled in the art, can be readily obtained by making the usual experiments, analyses, and tests.

It is of course impossible within the limits of a specification to describe each case of variation in proportion as the same may arise hereafter, nor is this essential to a due understanding of my invention by those skilled in the art. To convey all the knowledge requisite for the application of my improvement by such persons, it is necessary to do no more than give an illustration of the way in which I have actually in a certain case applied my invention. The analyses of the ore employed in this instance was per one hundred pounds, substantially as follows: silica, eight; alumina, three; magnesia, one; lime, two; phosphoric acid, 1.84; iron, fifty-nine.

In considering this application it will be borne in mind that the 1.84 phosphoric acid corresponds to 0.80 pounds of phosphorus and that in the blast-furnace substantially all the iron and almost all the phosphorus of the ore go into the pig metal, which, besides iron and phosphorus, contains some six per cent., more or less, of such constituents as carbon, silicon, manganese, &c., so that the fifty-nine pounds of iron mentioned in the above analyses as yielded by one hundred pounds of ore furnished about sixty-three pounds of pig metal containing 0.80 pounds of phosphorus, or very nearly 1.27 per cent. of phosphorus, or less. This phosphoric ore, smelted by itself, yielded a pig metal containing 1.125 per cent. of phosphorus and 3.17 per cent. carbon, mostly graphitic. The iron was of the grade frequently designated as No. 2 foundry, a fair quality of iron, but so weak as to break under two or three blows of a sledge-hammer. The slag accompanying it contained about forty-three per cent. of silica, the balance in alumina, lime, and magnesia. To three portions of this ore was mixed one portion of titaniferous ore containing eighteen to twenty per cent. titanic acid and about 57.90 per cent. iron. To this mixture enough phosphate of lime was added to raise its percentage in phosphoric acid to substantially the same figure as above stated in the phosphoric ore—viz., 1.84 per cent.—the titanic ore in this instance containing, as will be observed, practically as much iron as the phosphoric (57.90 per cent. against fifty-nine per cent.) and the titanic ore containing traces only or no phosphorus whatever. Therefore in the pig metal resulting from this mixture might have been expected substantially the same amount of phosphorus as in the pig produced as aforesaid from the phosphoric ore—viz., 1.27 per cent. The analysis of the pig metal resulting from this mixture treated in the ordinary well-known process of smelting was as follows: graphitic carbon, 3.54; combined carbon, 0.33; phosphorus, 1.229; titanium, 0.35; but this resultant pig metal might properly be graded as No. 1 foundry gray, a very tough and strong iron which required repeated blows from a sledge-hammer to break.

Again, my invention has been practically and successfully applied in another instance, as follows: To the aforesaid phosphoric ore was added apatite until the phosphoric acid in the resultant mixture equaled 4.80 per cent. This unusual and excessive amount of phosphoric acid corresponded to 2.13 pounds of phosphorus in sixty-three pounds of pig metal yielded by one hundred pounds of the mixture. From the smelting of this mixture was to be expected 3.36 per cent., more or less, of phosphorus in the resultant pig. The analysis of the pig actually gave 2.862 per cent. of phosphorus in the metal, which latter was extremely weak, breaking easily at the first blow of the sledge-hammer. The grade might properly be designated as between No. 2 and No. 3 foundry, almost a No. 2.

In the next instance two parts of the aforesaid highly-phosphoric mixture were added to one part of titaniferous ore of the following composition: silica, 1.53; titanic acid, 19.74; alumina, 3.50; lime, traces; magnesia, 1.50; oxid of iron, 73.62; phosphorus, none; metallic iron, 53.32, together with a sufficient amount of apatite to raise the percentage of phosphorus to be expected in the pig metal to 3.36 per cent or thereabout. This mixture was subjected simultaneously to the same smelting treatment as the aforesaid highly-phosphoric mixture, the two mixtures being treated in large crucibles placed side by side in a furnace with forced blast and exposed to the same firing for the same length of time and the treatment in each case simultaneously terminated.

In the case of the mixture with titaniferous ore the analysis of the resulting pig showed 3.229 per cent. of phosphorus and of titanium 0.47 per cent. The grade of this pig might have been properly designated as No. 2 foundry. The iron was quite strong and it required several blows from a sledge-hammer to break it. Its contained carbon was for the most part in the graphitic state, as in the case of the pig metal resulting from the merely phosphoric mixture aforesaid. The resultant slag analyzed in round numbers about as follows: silica, thirty-one; titanic acid, fourteen; alumina, seventeen; lime, twenty-eight; magnesia, ten; and it is interesting to bear in mind that this titaniferous ore, if smelted by itself, would have yielded an iron which, though characteristically tough and strong, would have been of the characteristic light steel-gray color and having nearly all its carbon in the combined state. Thus by my invention of applying titanic to the phosphoric ores, as aforesaid, not only may the resulting iron be produced of a very fair foundry-pig quality, but also of a grade properly designated as No. 2; and though in the instance in which one-third of titanic ore was added to the phosphoric ore the resulting metal lost one grade, being No. 2 instead of No. 1, as

in the case where only one-quarter of titaniferous ore was added to the mixture, nevertheless the resultant metal contained by far the greatest quantity of its carbon, as aforesaid, in the graphitic state. Thus the effect of my mixture is not only to improve the resultant pig-iron by counteracting the weakening effect of the phosphorus by the characteristic influence of the titanium on the iron, but also the phosphorus itself operates to influence the state in which is found the carbon contained in the metal, whereby such carbon is caused to exist in the iron in the graphitic state even in cases where so much as one-third of titaniferous ore is added to the mixture.

The foregoing instances demonstrate that even in cases where the excessive amount of three per cent. of phosphorus is found in the resultant pig-iron metal the action of the titanic admixture is so beneficial as to secure a satisfactory and vastly stronger and tougher iron, and I find in experimenting with other proportions of the two classes of ores referred to—viz., phosphoric and titaniferous ores, for instance, with twenty parts of titanic ore to eighty parts of phosphoric ore and forty parts of titanic ore to sixty parts of phosphoric ore, among others—that in each case it is easy after such use, trial, and experiment as would be made by any person skilled in the art to proportion the quantity of a given titanic ore to be added to a given phosphoric ore in order to secure the most satisfactory and economical results, analyses having first established the quantity of phosphoric acid in the phosphoric ores and of titanic acid in the titaniferous ores.

I am aware that the analysis of certain irons heretofore made disclose the presence of minute quantities of titanium and of phosphorus, as of numerous other elements, but such compounds in pig-iron have, so far as I know, been, prior to my invention, accidental and not the result of design or the combination of a titaniferous ore with a phosphoric ore with the express purpose of redeeming the latter and rendering it tough and adapted to the manufacture of steel.

I am also aware that it has been suggested that crude pig-iron may be dephosphorized by mixing it in a furnace, cupola, or refinery with ores or minerals containing a large percentage of titanium, as titanic iron ore or ilmenite, with the effect, so stated, that the phosphorus in the furnace, having greater affinity for the titanium or titanic acid than for iron, leaves the latter and passes off in the slag; also, that it has been recommended to improve the quality of cast-steel by melting it in a melting-pot or crucible with various preparations or combinations of "titanium," so called, in unspecified quantities, preference being expressly given to such elements as are free or nearly free of phosphorus; also, that it has been suggested that wrought-iron may be produced by intimately mixing with molten cast-iron solid oxidizing substances to act as detersives by combining with and carrying off impurities which it is stated would otherwise remain to the detriment of the product, and thus, for instance, where iron is desired to be "cold short" that phosphorus be employed for this purpose by using iron ores especially rich in that substance or phosphates of lime or any other substance into which phosphorus largely enters, and that it has been suggested that this alloying with iron of titanium in the proportion of about one-half per cent. of the latter to the weight of the former will give additional purity to the latter; also, that as an improvement in the manufacture of steel it has been suggested that some irons containing so much phosphorus as to render them unfit for manufacture into homogeneous or cast steel should be treated by expelling substantially all other substances, so as to leave the phosphorus in preponderance over any of them, so as to permit the phosphorus to unite with the iron in a homogeneous alloy and to that end charging into the open hearth of a reverberatory and regenerative gas-furnace a mixture of pig-iron, old steel rails, or other scrap-steel with other regenerative substances, the phosphorus contained in the materials of said charge being in the proportion of twenty-hundredths to fifty-hundredths of one per cent. of the weight of the iron, and that in cases where a slight deficiency in the proportion of phosphorus occurred then, if deemed expedient, some silicum, chromium, titanium, or other steelifying agent might be added to the charge in place of carbon to compensate the deficiency of phosphorus. None of these processes do I regard as constituting my present invention, which has, as aforesaid, relation to the redemption of phosphoric iron ores hitherto unavailable for the manufacture of steel by mixing and treating the same so as to produce a tough, though phosphoric, pig-iron, in an ordinary blast-furnace, together with titaniferous ores.

What I claim as new, and desire to secure by Letters Patent, is the following:

1. The process of producing out of iron ores containing phosphorus in such quantities as to render them unfit for purposes of good foundry-pig a tough phosphoric pig-iron, well adapted to good foundry purposes and without the brittleness and weakness characteristic of ordinary phosphoric iron, and containing titanium and also substantially all the phosphorus which was in said ore, which consists in mixing and smelting together in a blast-furnace, such phosphoric ore together with titaniferous ore, all substantially as and for the purposes described.

2. The process of producing out of iron ores containing phosphorus in quantities exceeding say fifty-hundredths of one per cent. of the weight of the ore, a tough phosphoric pig-iron, well adapted to good foundry purposes and without the brittleness and weakness characteristic of ordinary phosphoric iron,

and containing titanium and also substantially all the phosphorus which was in said ore, which consists in mixing and smelting together in a blast-furnace, such phosphoric ore together with titaniferous ore, substantially as and for the purposes described.

3. As an article of manufacture a tough phosphoric pig-iron free from the characteristic weakness and brittleness of ordinary phosphoric iron and well adapted to good foundry purposes, containing titanium, and also containing phosphorus in quantities not less than one and one-fourth per cent. of the weight of such pig-iron, all substantially as and for the purposes described.

AUGUSTE J. ROSSI.

Witnesses:
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