METHOD OF PRODUCING FERROUS METAL OF CONSTANT PROPERTIES FROM HETEROGENEOUS MIXTURES

Inventor: Henri Langagne, Tourcoing, France
Assignee: La Bonvarite, Louvroil, France
Filed: June 14, 1973
Appl. No.: 369,841

Foreign Application Priority Data
June 15, 1972 France 72,22936

U.S. Cl. 75/51; 75/59; 75/60
Int. Cl. C21c 7/00
Field of Search 75/51, 59, 60; 204/176

References Cited
UNITED STATES PATENTS
2,255,016 9/1941 Smith 75/57
3,251,680 5/1966 Goss 75/51
3,309,300 3/1967 Grosse 204/176
3,551,139 12/1970 Schokkenbrock 75/58
3,583,866 6/1971 Grenfell 75/60
3,603,571 9/1971 Geiger 75/43


ABSTRACT

A method of producing ferrous alloys, especially cast irons, having predetermined properties and of predetermined quality from heterogeneous raw materials with corrective additives, the quality of the final product being independent of the raw materials used. In a cupola charged with alternate layers of coke and raw materials and set in operation, ozone is continuously added in small amounts as well as a compound for liberating nitrogen, such as hydrogenated nitrogen compounds and organic nitrogenous compounds, and an halogen, such as methyl chloride or chlorobenzene. Liquidus temperature curves are plotted for given temperature and additions of steel, for obtaining the optimum liquidus temperature. The melting is continued as a function of the desired relationship of carbon equivalent, eutectic temperature and amounts of steel, for example, to be added, and tensile strength thereby maintaining the optimum liquidus temperature.

22 Claims, 2 Drawing Figures
METHOD OF PRODUCING FERROUS METAL OF CONSTANT PROPERTIES FROM HETEROGENEOUS MIXTURES

The present invention relates to improvements in the selective precision production of ferrous metals, such as cast iron and steel of predetermined properties, by melting heterogeneous raw materials. The method provides inter alia general means which, determined from the operating conditions of a given foundry, may be subsequently used for other foundries.

The invention also concerns the cast irons and steel obtained by this method.

Generally speaking, foundries are required to furnish, as economically as possible, metals having well-defined and constant chemical composition and physical characteristics corresponding to their intended use. In order to satisfy this requirement, it is necessary to have available means for reproducibly obtaining in a foundry a metal whose chemical composition falls in a narrow theoretical range and where principal physical properties are very close to the desired properties. For cast irons, these properties include, inter alia, tensile strength, Brinell hardness as well as the percentage of silicium which contributes to facility of subsequent machining. However, for raw materials for making cast iron, foundries dispose of very heterogeneous materials such as scrap iron, and steel and iron works rejects, to which there must be added fresh products like new foundry iron or foundry pig in order to render the former materials usable. It is naturally impossible at the beginning to obtain a sufficient chemical analysis of the rejects to be informed, for example, on the carbon and silicium content of the raw materials in order to be able to obtain the desired composition and characteristics.

By using such raw materials, in particular rejects, it has also been observed that the concentration of certain elements increases sometimes reaching considerable percentages which are generally undesirable. In the rejects there may be found, especially in manufactured products, copper, chromium, molybdenum, nickel, titanium, and the like. Other impurities originating, for example, in the ores, treatments and refractory linings of the foundry furnace, as well as incoherents may also be concentrated in the metal. Calcium, aluminium, zirconium, lithium, strontium and barium are cited by way of example. Now, all these impurities become more and more concentrated in the raw materials until they exceed a threshold level above which, irrespective of the origin of the raw materials, it is practically impossible to obtain the required physical properties.

Various attempts have already been made for overcoming these problems, but all the proposed solutions depend upon the rule-of-thumb experience of the founders which explains the irregularity of the results and the lack of reliability of the method heretofore applied.

One known method consists in using fresh foundry pig or iron to dilute at least a portion of the impurities of the rejects whose analysis is practically impossible. It is not surprising that for this reason alone the results are uncertain and variable, but this uncertainty and variation are further increased by the type of foundry pig or foundry iron used; indeed, nowadays there is introduced into the blast furnace a percentage of petroleum products, such as fuel oil, as fuel partially replacing the coke. It has been found that pig iron made in part with petroleum products is poorly suited for effecting the aforesaid dilution because endogenetic slag forms during melting and separates during cooling. In addition to this problem is the systematic inoculation of the steels, the killing by elements such as aluminium, titanium, lithium and zirconium, the use of tin for hardening the cast irons and the manufacture of wrought iron, the agglomeration of the sands by furanic resins; each phenomenon causes the concentration of numerous impurities and consequently substantial and unpredictable rejects.

It has also already been proposed to make corrections during melting, by the modification of the percentage of the fuel between charges or by correction in the ladle by adding graphite and silicium when the melt has become too strongly oxidizing. These corrective changes are also effected empirically, and naturally they only react after the melting of the preceding charges, i.e., after the observed operating mishap. A large amount of metal which does not have the anticipated and desired characteristics is thereby rendered unusable. In any event, the empirical corrective charges usually called "false charges," do not avoid the formation of endogenetic slag, the cause of numerous rejects, regardless of the value of the carbon equivalent: there has been observed, amongst other things, the fall of the mechanical strength characteristics by the looseness of the grain structure owing to the presence of the impurities or slag, a significant increase in the tendency to form shrinkage cavities or holes and cracks, and excessive porosity.

A method furnishing the cupola with very homogeneous high grade pig is also known which enables the reduction of rejects, by introducing into the cupola a certain amount of cetene-forming agent; this operational industrial method is further advantageous by its flexibility in operation, but it does not eliminate the difficulties due to the heterogeneity of the constituents of the mixture treated.

One could obviously consider (as this was in fact the object of many known processes) that the perfect knowledge of the raw materials and their purity would enable the manufacture of the cast iron meeting the precision and substantially reproducible conditions; however, it has never been contemplated to provide the founders with means for putting the various installations under optimum conditions in a practically automatic way for providing a given cast iron having precise characteristics from heterogeneous materials of different origins.

Such an actual industrialization of cast iron processing is in fact the principal object of the invention which in addition proposes to produce very high strength lamellar cast iron which is readily cast and easily machined, from usual heterogeneous raw materials.

Starting from the fact that — as is known for raw materials and a given foundry — the variation of the carbon equivalent (CE) as a function of the liquidus temperature (T0,2) is linear and the tensile strength varies with the carbon equivalent, the inventor undertook numerous tests and studies with the aforesaid object in mind; first of all, these studies showed him that the linear variation of CE as as function of liquidus temperature was purely theoretical and that the random variations of the corresponding straight line of tensile strength resulted from the impurities and various origins of the raw materials utilized. It was therefore possible to conclude that these variations ex-
plained, in fact, the problems associated with the manufacture of cast iron according to known methods. From the basic general study for the invention therefore developed from this interpretation of known phenomena and problems the following conclusions: there should be a way of using heterogeneous raw materials for obtaining with great precision a metal of predetermined physical properties and that the raw materials having a large concentration of impurities as well as fresh pig iron processed at least in part with petroleum products could be used and lead to a normal manufacture in spite of their disadvantages. In this, instead of being satisfied, as is usually the case in foundries, with adapting the melt-temperature situation to the required conditions a posteriori and charge by charge by empirical corrections and necessarily delayed action the invention provides to utilize the known drawbacks and problems in order to determine, first of all, an optimum liquidus temperature for a desired carbon equivalent and tensile strength and then bring about a change in the melt as a function of this temperature and the results of these corrections which have a nearly immediate effect, thus enabling the manufacture of the end product in a reliable and reproducible manner.

The method of the invention for producing cast iron of predetermined quality in starting from heterogeneous raw materials, by melting the said materials with corrective additives of the constituents is characterized in that after charging a furnace, such as a cupola, in a known manner with alternative layers of fuel (coke) and raw materials, it is started up, introduced into the cupola on the one hand small amounts of ozone and on the other hand at least one compound for liberating nitrogen and a halogen at the melting temperature, it is determined for a given temperature and by introducing different amounts of one of the constituents, steel for example, the melting curves corresponding to different liquidus temperatures for a selected range as a function of the eutectic temperature, it is fixed from these curves the amount of steel to be added to any mixture of the available raw materials for a given carbon equivalent C.E. in order to provide the optimum liquidus temperature corresponding to the mixture and to the tensile strength to which it corresponds, the melting is continued as a function of the desired relationship of carbon equivalent, eutectic temperature, addition of steel, tensile strength so as to directly maintain the optimal temperature, i.e., for elaborating a cast iron of constant quality, independent of the heterogeneous materials employed.

By studying the numerous tests effectuated according to the aforesaid interpretation, Inventor has noted the unexpected fact that when the curves which will be precised hereafter and which correspond to a given foundry were defined, it was possible to use these results for any other foundry. This is a great advantage for reliable manufacture of cast iron of predetermined grade since the invention thereby enables in all cases mastery of the liquidus temperature of the metal and to obtain, so to speak, any predetermined value of the carbon equivalent and further tensile strength values which were not to be foreseen for cast iron.

The treatment of the impurities which is a selective refining of the raw material not only enables the optimum melting temperature to be subsequently maintained, but also taking into account the foundry standardization according to the invention, permits a recarburization or decarburization of the melt while, if desired, attaining values of carbon equivalent of the eutectic point ranging from 4.20 to 4.60 corresponding to the manufacture of lamellar graphite cast iron and up to a liquidus temperature of 1,300°C: it is known that these zones are now considered as the range of malleable cast iron.

Other features concerning the treatment of impurities are as follows:

When it is desired to obtain a product whose percentage carbon is greater than the sum of a carbon percent of the raw materials in the furnace, a compound derived from the distillation of products of plant (vegetable) origin, selected from the group of coal, wood and natural resins, is introduced.

In case a product is desired whose total carbon percentage is less than the sum of the carbon in the raw materials in the furnace, an oxygenated compound liberating oxygen at the melting temperature is introduced. Hence, distinct means are available for raising and lowering the liquidus temperature to the optimum temperature during the entire melting operation.

In order to carry out this refining operation which is essentially to "standardize" the foundry one may use a mixture of compounds separately liberating nitrogen and chlorine or a single compound liberating both cases. In this case it is necessary to release the gases in situ in the molten metal by means of a compound liberating the gas since the simple gas mixed with air for combustion does not yield good results.

Amongst preferred compounds for liberating nitrogen, the following may be cited, as examples: ammonia, hydrazine salts and organic nitro-derivatives in general. Solid hydrazine salts are preferably used in the ladle whereas the other liquid or gaseous compounds are injected into the combustion-supporting air: it has been found that carbides, nitrates or carbonitrates of titanium, zirconium, or aluminum, for example, were neutralized by the nitrogen liberated directly in the metal. Nitrobenzene and hydrazine give very good results in this case.

The concentrations of aluminium, zirconium, magnesium, calcium, silicon, titanium, chromium, manganese, nickel and iron oxides and sulfides are reduced in large proportions by the action of the chlorine-liberating compound. These oxides and sulfides are in part eliminated in the slag while the remainder is neutralized. It has been found that liberated fluorine gives the same results, and moreover it facilitates the rise of the oxides and sulfides in the form of slag.

The organic or inorganic products liberating the chlorine which provides satisfaction are slightly chlorinated. The process may be simplified in its whole advantageously by using organic chlorinated solvents capable of dissolving the products of distillation of coals, wood and natural resins. In particular, methyl chloride, chlorobenzene and chloronitrobenzene have given total satisfaction. The chloronitrobenzene has the advantage of being able to react during the refining as sole compound. In certain cases it is possible to use an oxyhydrogenated compound also liberating oxygen at the melting temperature.

In case the raw materials contain a substantial proportion of copper, it would be advisable to add to the refining agent a calcium or sodium acetate in the ratio of 10% of the charges of Fluxes.

Since the optimum liquidus temperature determined by the curves for a given value of tensile strength ought
to be maintained during melting or at the very least in the final phase, it is possible, according to the invention and to the requirements, to increase the liquidus temperature and then decarburize the metal, or reduce the liquidus temperature and then recarburize, as it appears from the curves showing the relationship between the carbon equivalent CE and the liquidus temperature ThEq. Such recarburization or decarburization thus provide by controlling the melt a metal whose total percentage of carbon is at will, greater or less than the total carbon percentage of the materials in the furnace, including thereby the natural recarburization in the cupola.

For recarburization, the best results are obtained with compounds coming from the distillation of products of plant origin, selected from the group of coal, wood and natural resins. An injection of coal tar or wood tar produced remarkable results. The following has been observed: a rapid and sensitive recarburization, an aliphagic effect ascertained by the reduction of the tempering and the tendency to form cementite, a reduction of the sensitivity of the part depending on its thickness, a substantial increase in the tensile strength as well as the absence of endogenous slag formation.

According to the invention, the recarburization is preferably carried out most often at the same time as the refining: for this purpose the selection of the compounds is made by taking into account the following observations: the injection of certain compounds coming from the distillation of products of plant origin depending on their origin and physical properties, may bring about the casing of these compounds at the end of the nozzles by coking; however, this problem is avoided when a distillate is selected from the light oil or a heavy oil fraction or even a distillation residue when diluted in an appropriate solvent. Among the solvents yielding good results, the following may be mentioned: cyclohexane, toluol and anidolol. Nevertheless, there is a preference for the above-mentioned organic chlorinated and nitrochlorinated compounds which are used at the refining agent as well as the solvent. When recarburization is necessary, it suffices to dilute the composition obtained from distillation in methyl chloride, chlorobenzene or fluorobenzene.

Amongst the compounds which have been found satisfactory, there may be mentioned coal tar or wood tar, chosen from light, medium or heavy oil fractions, as well as distillation residues or distillates of natural resins such as pine resin or rosins. The residues from the manufacture of turpentine also yield good results. All these products are soluble in the above mentioned solvents.

Other carbonaceous products were tested without achieving good results. They are often solids which are difficult to measure in injection, such as charcoal powder, small coke, lean coal dust and powder graphite, there is practically no recarburization. The same observation was made when introducing petroleum products such as Diesel oil which results only in coke savings by merely constituting a source of heat.

The introduction of the recarburizers diluted in a natural gas, (butane or propane) jet or burner has the advantage of reducing the oxidizing power of the gases burned while at the same time increasing the flame temperature of the jet or burner.

By way of example, 2 to 4 liters of a mixture containing 50% coal or wood tar light oil fraction by weight with one of the solvents or refining agents, mentioned above, may be introduced per metric ton of metal.

Ozone, when controlled, is a compound liberating oxygen at the melting temperature and giving excellent results. With air enriched by 10% ozone it becomes possible to decrease the carbon equivalent to 0.6%. For assuring this control of ozone, it is advantageous to introduce at the same time as the ozone an additive tending to raise the decomposition temperature of ozone to a value close to the melting temperature, in order to avoid a too rapid decomposition of ozone and thereby obtain a better decarburization, isopropyl oxide and turpentine are possible additives. The oxidation of metalloids, particularly silicium and manganese, remain within reasonable limits, below 15%.

Combustion-supporting air is treated by a bank comprising a plurality of ozone generating elements thereby enabling a more or less energetic decarburization. It is found that the carbon equivalent decreases rapidly with air saturated with ozone. Thus, a liquidus temperature which is too low may be raised towards the optimum liquidus temperature.

Other compounds for liberating oxygen at the melting temperature which give equally good results, are oxygenated organic or inorganic salts such as halogenates or organic ether oxides. Oxyluorinated salts, such as chlorates, have the advantage of acting as both decarburizer and refining agent as indicated above.

The foregoing which was obtained for a given foundry and a particular set of heterogeneous materials has been found to be directly applicable, mutatis mutandis to all foundries and raw materials.

Before describing the method according to the invention in detail it should be recalled, first of all, that by the term cast iron it is designated a ferrous alloy containing carbon in an amount greater than the maximum solubility of this element in iron. Moreover, it is known that the maximum solubility in an iron-carbon binary system is attained at 1147°C, the theoretical value is 2.06% which gives the "unstable" — or stable — system (white pig iron). But the amount of carbon is less when the iron contains substantial amounts of aliphagic elements, silicium especially. The iron then cools according to the "stable" system; the eutectic temperature is 1153°C and the percentage of carbon is no more than 2.03%. Therefore, between the unstable and stable systems the eutectic concentration (carbon saturation) varies between 4.25 and 4.30.

The formula giving the carbon equivalent (C.E.) enables the comparison of an iron alloy containing carbon, silicium and phosphorus with an iron-carbon binary system. Starting with a cast iron of the same chemical composition, viz. 3.47% total carbon, 2.40% silicium and 0.10% phosphorus, it is said — depending on the country or the technician — that 1% silicium is equivalent to 0.33, 0.25 or 0.22 carbon, i.e., the eutectic concentration or carbon equivalent has values 4.30, 4.05 or 3.98 respectively depending on the formula employed, which in the U.S.A. is:

\[
CE = C + \frac{Si}{3} + \frac{P}{3} \quad \text{where} \quad Si = 0.33 \, C
\]

\[
CE = 4.30 = 3.47 + \frac{2.40}{3} + \frac{0.10}{3}
\]

in the U.K.
in France (according to Renault) is:

\[
CE = C + \frac{Si}{4} + \frac{P}{2} \quad \text{where} \quad Si = 0.25C
\]

\[
CE = 4.12 = 3.47 + \frac{2.40}{4} + \frac{0.10}{2}
\]

Therefore, depending on which of the formulae one uses, the English and French points of carbon equivalents, are respectively 0.18 and 0.25 below the point 4.30 (that of the American formula). The example described hereinafter is based on the last-mentioned formula (CE = 4.30) but corresponding results are attained with the English and French formulae. The remark is here to be made, that the great divergence between the interpretations of technicians should be noted which confirms that there are unknown factors to be discovered, precised and mastered.

The tests carried out have established that the eutectic concentration point is not in reality fixed but varies according to the manner of melting, nature of raw materials, etc., furthermore the tests show that when the eutectic concentration increases, the quality of the metal also increases.

According to the invention, the carbon equivalent is calculated as a function of the melting rate expressed in metric tons/hour/sq.decimeter (D²) of the section of the cupola, and the percentage steel of the metal charges uniformly distributed between 0% and 100% for the useful range of liquidus temperature T_{liq} between 1150°C and 1300°C for lamellar graphite cast irons. Considering a melting rate between 4.6 D² and 6.5 D² for a production rate between 5.6 D² and 6 D², the throughput rate in metric tons/hour for a cupola having a diameter of 1 meter is as follows:

<table>
<thead>
<tr>
<th>(index)</th>
<th>melting rate</th>
<th>production P</th>
<th>coefficient A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.6 D²</td>
<td>5.6 D²</td>
<td>6.0 D²</td>
</tr>
<tr>
<td></td>
<td>4.6 MT</td>
<td>5.6 MT</td>
<td>6.0 MT</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A is the slope of the melting curves and is equal to:

\[ P = \text{distance} \times 3.65 \]

The coefficient A can be determined according to the formula:

\[ A = \frac{\text{distance}}{\text{ac} \%} \]

where ac% indicates the percent of steel.

The distance (which may be called "liquidus distance") is the difference between the liquidus temperature of the mixture and the eutectic liquidus temperature which in the present example was chosen at 1150°C, which is the average of 1147°C and 1153°C respectively corresponding to the unstable and stable systems respectively.

Finally the diagram or graph shown in FIG. 2 is constructed which enables the control of the operation of the cupola in order to obtain a given cast iron. This graph shows for given initial eutectic liquidus temperature, coefficients A, and production as well as the correlations between the melting rate, the percentage steel added (ac%) the liquidus distance, liquidus temperature and carbon equivalent relative to the initial eutectic point.

D. is the internal diameter of a cupola expressed in meters and measured at a distance between 20 and 30 cm above the tuyeres. The coefficients 4.7 - 5.6 - 6.0 - 6.8 represent the production according to the said coefficients: it is said that a cupola having a diameter of one meter, i.e., \( 1 \times 1 = D^2 \), produces 4.7MT, 5.6MT, 6.0MT, 6.8MT/hour when enough air is provided in order to ensure the production of 4.7 D², 5.6 D², 6 D², 6.8 D².

The production is controlled by the charging rate of the furnace: the cupola having a diameter of 1 meter operating at 6 D² absorbs 10 charges of 600 kg per hour, i.e., a charge every 6 minutes; foundries commonly define the cupola by D². The coefficient of production P expressed as D² varies in practice between about 4.5 and 6.8 for normal melting and the relationships with the corresponding coefficients A are obtained as follows:

In the graph (FIG. 2) increasing values of steel are indicated on the abscissa; to facilitate the reading of the curves a double distance has been chosen for the values of steel compared to the corresponding distances, liquidus temperature and carbon equivalent.

According to the scale in the graph, 10°C liquidus temperature is represented by 10 mm and 10% steel is represented by 20 mm; thus 10 mm along the ordinate gives a change in the coefficient A of 0.1 on the abscissa at 100%. In order to plot the ends of the curves it suffices to mark 100 mm on the ordinate to obtain the curve A = 1; 140 mm for the curve A = 1.4; 150 mm for the curve A = 1.5 and so on. The origin O corresponds to 0% steel on the abscissa and on the ordinate, liquidus temperature which was chosen equal to 1150°C, eutectic concentration point which is valued at a carbon equivalent of 4.3. The liquidus temperatures along the ordinate are transformed into distances relative to the origin; by dividing this distance by 100 and multiplying it by the coefficient 0.9, the decreasing values of carbon equivalent are obtained which are to be subtracted from the value of the carbon equivalent at the origin which in this example is 4.30.

For example, along the upper curve (Aₛ) for a value of 55% steel on the abscissa we read a liquidus temperature of 1260°C, a liquidus distance (dist.) of 110°, and carbon equivalent (CE) less 0.99 on the ordinate. Indeed 1260°C liquidus minus 1150°C at the origin gives 110° as the distance; now it is known that the coefficient A is

\[ \text{Dist} \quad \text{ac} \% \]
that is, in the present example:

\[ A = \frac{110 \text{(dist.)}}{55\% \text{ (steel)}} = 2. \]

Along the curve \( A = 2 \) for 100% steel, a liquidus temperature of 1350°C is obtained. Therefore, \( A \times \text{ac%} = \text{distance liquidus} = 2 \times 100 = 200 \) (dist. liquidus) that is 1150°C + 200 = 1350°C liquidus temperature. The corresponding CE is:

\[ 200 \times 0.9 = 1.8; \]

thus, the CE corresponding to the liquidus temperature of 1350°C is 4.30 minus 1.8 = 2.5.

For plotting the curve \( A = 1 \) which is not shown on the graph, the formula dist. liquidus = \( A \times \text{ac%} \) is used. For 100% steel one gets: \( A = 1 \times 100 = 100 \); it suffices to mark 100 mm starting from the abscissa.

Now marking on this straight line the ordinate corresponding to 55%, the corresponding values of liquidus temperature and CE are calculated; the formula yields: dist. liq. = 55 × 1 = 55. The liquidus temperature is 1150°C at the origin + 55 (dist. liq.) = 1205°C; the equivalent of carbon for this liquidus temperature 1205°C is:

\[ 55 \times 0.9 = 0.495 \]

At 1150°C, the CE is 4.3; at 1205°C, the CE is therefore 4.3 - 4.95 = 3.805. Therefore, a coefficient \( A \) at the liquidus temperature of 1205°C with a charge of 55% steel corresponds to a carbon equivalent for an eutectic carbon equivalent of 4.3.

There will now be checked the curve \( A \) for \( A = 1.3 \) which corresponds to a melt balanced in steel and a production \( P = 4.7 \text{D}^2 \), i.e., 4.7 MT for a cupula 1 meter in diameter (or a production of 2.35 MT for a cupula 71 meters in diameter, or \( D^2 = 0.5 \)):

in effect, \( P = 4.7 \times 0.5 \text{D}^2 = 2.35 \text{MT} \)

Along this curve \( A \), at the coefficient \( A = 1.3 \) for 100% steel the distance read is:

\[ \text{liq. dist.} = A \times \text{ac%} = 1.30 \times 100 = 130 \]

Therefore, liquidus temperature for 100% steel is:

\[ 1150°C + 130 = 1280°C \]

The corresponding carbon equivalent is:

\[ 130 \times 0.9 = 1.17 \]

at 1280°C the carbon equivalent is 4.3 - 1.17 = 3.13

If the liquidus temperature is wanted which corresponds to 55% steel in the charges for \( A = 1.3 \):

\[ \text{liquidus distance} = 1.3 \times 55 = 71.5 \]

liquidus temperature = 1150°C + 71.5 = 1221.5°C, rounded up to 1222°C.

The CE corresponding to a liquidus temperature of 1222°C is:

\[ CE = \frac{71.5}{100} \times 0.9 = 0.643 \]

CE at 1222°C = 4.3 - 0.643 = 3.657

For the curve \( A_x \), \( A_x^2 = 1.5 \) which corresponds to a production \( P = 5.6 \text{D}^2 \) or 5.6MT for a cupula 1 meter in diameter (2.8MT for a cupula 0.71 meters in diameter) at 100% steel; dist. liq. = 1.5 × 100 = 150 T.liq. = 1150°C + 60 = 1300°C

\[ CE = \frac{150}{100} \times 0.9 = 1.35; \text{CE at a T.liq of 1300°C} = 4.30 - 1.35 = 2.95 \]

For 55% steel one obtains:

\[ \text{dist. liq.} = A = 1.5 \times 55 = 82.5 \]

T.liq. = 1150°C + 82.5 = 1232.5°C. or 1223°C when rounded up.

\[ CE = \frac{\text{dist.liq.}}{100} \times 0.9 = \frac{82.5}{100} \times 0.9 = 0.74 \]

CE at liquidus 1233°C = 4.3 - 0.742 = 3.538

For the curve \( A_y \), \( A = 1.7 \) which represents a cupula operating at a coefficient of production of \( 6 \text{D}^2 \)

The ordinate corresponding to 100% is always calculated from the relationship dist.liq. = \( A \times \text{ac%} \), or

\[ 1.7 \times 100 = 170 \text{ dist.liq.} \]

the corresponding T.liq. = 1150°C + 170 = 1320°C

\[ CE = \frac{170}{100} \times 0.9 = 1.53 \]

the CE at a liquidus 1320°C will be: 4.3 - 1.53 = 2.77.

On the same curve, when using 55% steel, the liquidus temperature for the charge is:

\[ 1.7 \times 55 = 93.5°C \]

T.liq. = 1150°C + 93.5 = 1243.5°C, or 1244°C when rounded up.

\[ CE = \frac{93.5}{100} \times 0.9 = 0.841 \]

CE at a 1244°C liquidus is 4.30 - 0.841 = 3.46.

The tensile strength will be calculated for this cast iron assuming the value of the cast iron B (basis cast) has a tensile strength equal to 16 kg/mm² for a test piece having a diameter \( \phi = 30 \text{mm} \). This value is measured at the eutectic carbon equivalent of 4.3. The tensile strength is expressed by the equation \( RT = ax + b \).

The tensile strength curve RT (FIG. 1 curves) I is plotted taking as the origin the values of B (RT of the basic cast iron at the eutectic) = 16 \text{kg/mm}^2 for the curve CE = 4.30 at the eutectic of 1150°C and B = 20 \text{kg/mm}^2 for the curve II' at the eutectic carbon equivalent of 4.40. Each drop of 0.10 in carbon equivalent increases the tensile strength 3.16 \text{kg/mm}²; one degree C of the liquidus temperature therefore increases the tensile strength by 0.316 \text{kg/mm}².

FIG. 1 was obtained by a series of carefully effected meltings. By taking the point 1205°C on the curve of 4.30 CE in FIG. 1, the distance is 1205 - 1150 = 55, it is simply necessary to multiply 0.316 kg by 55 which equals 17.38 \text{kg/mm}² and add this result to the basis value B = 16, which gives: 17 + 16 = 33.38 \text{kg/mm}² if melting occurred along the curve eutectic CE = 4.40, the following is obtained:
For the cast iron manufactured at a liquidus temperature of 1244°C, \( x = \) dist liq = 1244 - 1150 = 94°C. The value of \( a \) is 0.316 kg, \( ax = 94 \times 0.316 = 29.70 \) kg/mm². 

\[
ax + B = 20 kg\text{kg/m²} + 16 = 45.7 kg.
\]

The linear equation for the tensile strength is therefore \( RT = 0.316 \) (liquidus distance) + B. 

The value of B is similarly calculated for an iron cast at the liquidus temperature of 1233°C and manufactured with 55% steel, whereby the cupola operates with a coefficient \( A = 1.5 \); the test piece has a tensile strength of 42.1 kg/mm². 

calculation of the liquidus distance = 1233 - 1150 = 83°C. 

value of the tensile strength obtained by the liquidus distance 0.315 kg x 83 = 26.14 kg/mm²; 

the value of B at the eutectic is: 

\[
B = RT - ax, \text{ or } 42.30 - 26.14 = 15.96 \text{ kg/mm}² (B = 16kg/mm² rounded). 
\]

It is therefore seen that the curves of FIGS. 1 and 2 enable first the calculation and then the control of all the elements of a melt, and therefore the moment at which the decarbonization of the recarburization is to be undertaken, and the determination of the liquidus temperature of the molten metal at the moment of tapping. 

It should be noted that the equations giving the carbon equivalent 

\[
CE = \left( \frac{T_{liq} - 1150}{100} \right) \times 0.9 = CE_{eut} 
\]

tensile strength RT = 0.315 (dist. liq) + B are independent of the particular foundry, which confirms the general industrial nature of the method according to the invention. 

It is to be added that the graph of FIG. 2 correlates four curves, \( A_1, A_2, A_3, A_4 \), having the coefficients: 

\[
A_1 = 1.3 \text{ for a production } P = 4.7 D² \\
A_2 = 0.5 \text{ for a production } P = 5.6 D² \\
A_3 = 0.7 \text{ for a production } P = 6 D² \\
A_4 = 2.0 \text{ for a production } P = 6.8 D² 
\]

It should not be forgotten that according to conventional methods the production \( P \) in \( D² \) is an adjustment left up to the cupola founder who controls the cupola by feeding more or less combustion-supporting air. If he "feels" that the melting is not rapid enough, he goes from 5.6 to 6 \( D² \) by increasing the flow rate of air, but he does actually not know the liquidus temperatures of the molten metal, he only knows that in general his cupola recarbonizes about 2.8% the charges of steel and that if he increases production, the cupola recarbonizes a little less, but it is impossible for the founder to draw conclusions concerning the various corrections (materials, coke, melting rate, etc.) to be effected. 

Now, this becomes possible with the present method. 

If recarburization is undertaken, one must know that the melting rate \( P \cdot D² \) does not vary; assuming the cupola is adjusted for a production \( P = 6 D² \) with a coefficient \( A = 1.7 \), the production remains 6 \( D² \) but the coefficient drops in proportion to the flow rate of recarburizer, i.e., from \( A = 1.7 \) to \( A = 1.6 \) and then to \( A = 1.5 \) which means that the carbon equivalent is going to increase in the same proportion. 

The carbon equivalent at 1150°C goes from 4.30 to 4.40 and then to 4.50; according to this rule, the values of B will increase successively from B = 16 to B = 18 and then to B = 20.

If decarburization is proceeded, the operation is reversed, i.e., the coefficient is increased from A = 1.7 to A = 1.9 etc.; as the coefficient \( ax \) (see supra) increases in the same proportions, the carbon equivalent will decrease but the eutectic carbon equivalent will remain 4.30. In short, it could be said that when the coefficient A increases, it is as if the percentage of steel in the charges were increased and when the coefficient A decreases it is as if the percentage of steel in the charges were decreased. 

It must also be noted that when the air is enriched in oxygen by 0.6% to 1.2% (i.e., the percentage of oxygen goes from 21 to 23.5%) the production \( P \) is increased from 1.9 \( D² \) for 1.2% oxygen, and it is possible to operate above the critical level of 6.8 \( D² \), and without difficulty up to 8.7 \( D² \). Then, the liquidus temperatures are calculated on the curve \( A = 2 \) if the same proportion of fuel is maintained between the charges as for the melting at 6.8 \( D² \). 

The preparatory step — which is the refining of the materials — therefore enables subsequent melting with complete certainty, a practically immediate effectiveness of the corrections which corresponds to savings in time and great economy by the consistency of the quality and the substantially total elimination of rejects. 

Generally, it is advantageous to proceed in the following manner: 

At the beginning of melting, in case that the optimum liquidus temperature must be maintained at 1217°C, the blast air is therefore enriched with oxygen (7 to 10%) while also injecting at the tuyeres, for example, a mixture of fluorobenzene, chloronitrobenzene and isopropyl etheroxide. It is found that after a quarter of an hour to a half-hour the liquidus temperature reaches the optimum temperature of 1217°C. The production of ozone is then stopped while carrying on the refining. If the liquidus temperature starts to rise, recarburization is brought into play by using, for example, a tar diluted in chlorobenzene and fluorobenzene. 

The amounts of recarburizer to be injected will be 2 to 4 liters per metric ton of metal in order to avoid coking at the injector. 

As soon as the optimum temperature is reached, the recarburization is stopped and if, following a corrective charge "false charge" for re-establishing the equilibrium in the heights of the layers, the liquidus temperature falls once again, the feeding of ozone is started again. 

The metal manufactured by this method has astonishing foundry and physical properties. The metal becomes very sensitive to inoculation, 0.05% of an inoculant increases its characteristics by 3 kg/mm², with 0.10% it gains 5 kg/mm². The metal keeps its fluidity in the ladle, even after one hour irrespective of its carbon equivalent. The finely divided graphite gives it excellent friction properties. The perlite is very regular in parallel lamellae. The cementite is in bands narrower than the ferrite in the ratio of 1 to 2. Examined under an electron microscope the perlite observed in a jet piece having diameter of 30 and 300 practically maintains the same structure. Machining is effected in considerably less time and with considerably less tool wear. 

The metal is more creep resistant than steel. Flame hardening gives it a Brinell hardness of more than 550; and, the hardened surface is rather insensitive to scaling and shock. The resilience is 0.85 for cast irons having a tensile strength of 35 kg/mm²; it encreases to more than 1.9 for cast irons having a tensile strength of
3,928,022

55–60 kg/mm². The shear strength is greater by 2 to 3 kg up to a tensile strength 50 kg/mm², above 50 kg/mm², the shear strength is the same as the tensile strength.

The compressive strength is 5 times the tensile strength. A 10 mm hole drilled at 10 mm from the edge of a 60 mm bar resisted up to a pressure of 1000 bars. At a depth of 10 mm, the metal was absolutely freon and vacuum-tight.

By way of example, the results of 12 melts will now be given in the attached table. Six melts were carried out with recarburization and six with decarburization.

In order to appreciate in each of these two cases the role of the invention, three different test samplings were effected as follows:

1. an untreated test piece which was not subjected to refining or recarburization;
2. a test piece which was only subjected to recarburization; this test piece was taken just before the refining was begun; and
3. a test piece which was subjected to both refining and recarburization.

The following table shows with respect to melts 1–6 compared to the untreated test piece that with recarburization there is a total gain of carbon of 0.1 to 0.4%. The tensile strengths obtained are close to the sought-

<table>
<thead>
<tr>
<th>RECARBURIZATION</th>
<th>REFINING AND</th>
<th>RECARBURIZATION ONLY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50% steel</td>
<td>80% steel</td>
</tr>
<tr>
<td>desired tensile</td>
<td>30 36 38 40</td>
<td>43 47 30 36 38 40 43</td>
</tr>
<tr>
<td>strength</td>
<td>25 32 37 39</td>
<td>41 45 33 35 37 39</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>17 20 23 26</td>
<td>29 32 35 38 40 43</td>
</tr>
<tr>
<td>obtained</td>
<td>85 1205 1230 1240 1250 1260</td>
<td>1185 1205 1230 1240 1250 1260</td>
</tr>
<tr>
<td>(kg/mm²)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquidus</td>
<td>187 1208 1231 1244 1253 1262</td>
<td>1180 1201 1228 1235 1247 1254</td>
</tr>
<tr>
<td>temperature</td>
<td>4.10 4.03 3.78 3.64 3.60</td>
<td>3.51 3.67 3.26</td>
</tr>
<tr>
<td>obtained °C</td>
<td>3.26 4.13 3.95 3.68 3.63 3.57 3.50 3.40</td>
<td>3.20 2.90 2.75 2.70 2.55</td>
</tr>
<tr>
<td>Total carbone</td>
<td>3.20 3.00 2.95 2.94 2.90 2.85 2.72 2.55</td>
<td>3.33 3.15 2.88 2.83 2.56</td>
</tr>
</tbody>
</table>

What we claim is: 1. A method of producing cast irons having predeter-

mined properties from heterogeneous raw materials by melting said raw materials with corrective additives, comprising the steps of charging a furnace with alternate layers of fuel and raw materials, starting the operation of the furnace, continuously introducing ozone into the furnace as well as at least one compound liberating nitrogen and a halogen at the melting tempera-

ture of the raw materials, determining melting curves corresponding to different liquidus temperatures for a select range of raw materials as a function of the eutec-

after tensile strengths. It was found that for substantially equal liquidus temperatures, the tensile strength has substantially increased for the same percentage of steel.

If the effect of refining is sought, by comparing the results of the test pieces 1–6 with the test pieces 1–6', it is seen that the refining usually increases the tensile strength by 2–4 kg/mm². The foundry properties are always improved when refining is carried out simultaneously with recarburization.

It will be noted that by comparing, for example, the values of total carbone for 80% steel that the recarburiza-

tion is less effective than when there is no refining.

With respect to the results after decarburization in combination with refining, it is likewise noted that the tensile strengths are increasing when one goes from the untreated test piece to the test piece merely decarbur-

ized and then to the decarburized and refined test piece. The combination of decarburization and refining gives the best foundry properties. By comparing the melt 12' with the untreated test piece, it is seen that for the same percentage of steel and the same liquidus temperature, the tensile strengths increase from 37 kg/mm² to 54.6 kg/mm² respectively.

It must further be added and numerous test show, that the refining improves the sensitivity of the metals of classical inoculents. In this way, there is also substantial increase in the tensile strength as well as reduction of the sensitivity relative to depth.

The tests have shown that the liquidus curves are linear ones and that, according to the origin of the cast iron or to the nature of melting, difference CE are attained for same T liquidus; therefore, it is clear that the eutectic concentration is a variable one, which explains the differences and divergences above referred to.
tic temperature by introducing different amounts of one constituent of the raw materials for a given temperature and plotting a diagram thereof, determining from this diagram the amount of said one of the raw materials to be added to any mixture of available raw materials for a given carbon equivalent in view of obtaining the optimum liquidus temperature corresponding to said mixture and the corresponding tensile strength, continuing the melting as a function of the desired relationship of carbon equivalent, eutectic temperature, amounts of said one of the raw materials to be added and tensile strength, thereby directly maintaining the optimum temperature for the desired production.

2. A method according to claim 1, in which the compound liberating nitrogen and the compound liberating halogen is in fluid form and is introduced into the furnace with combustion-supporting air.

3. A method according to claim 1, in which a separate nitrogen-liberating compound and a separate halogen-liberating compound are provided.

4. A method according to claim 3, in which the nitrogen-liberating compound is a member of the group consisting of hydrogenated nitrogen compound, including ammonia and hydrazines; and organic nitrogenous compounds, including nitrobenzene and organic nitrated derivatives.

5. A method according to claim 3, in which the halogen-liberating compound also liberates oxygen at the melting temperature.

6. A method according to claim 3, in which the halogen-liberating compound is a solvent of the group consisting of products of distillation of coal, wood and natural resins.

7. A method according to claim 6, in which the halogen-liberating compound is at least one member of the group consisting of methyl chloride, chlorobenzene and fluorobenzene.

8. A method according to claim 1, in which the compound liberating nitrogen and the halogen is an organic monochlorated nitrated derivative.

9. A method according to claim 1, further comprising, for obtaining a ferrous alloy in which the carbon content is greater than the sum of the carbon content of the raw materials charged in the furnace, introducing a compound derived from the products of distillation of plant origin of the group consisting of coal, wood and natural resins.

10. A method according to claim 1, further comprising, for obtaining a ferrous alloy in which the carbon content is less than the sum of the carbon content of the raw materials charged in the furnace, introducing into the melt an oxygenated compound liberating oxygen at the melting temperature.

11. A method according to claim 1, in which at least one of the compounds liberating oxygen and the halogen is in solution in a solvent avoiding coking during injection.

12. A method according to claim 11, in which the solvent is a chlorated compound liberating chlorine at the melting temperature.

13. A method according to claim 11, in which the solvent is a member of the group consisting of cyclohexane, toluol and xylol for compounds derived from the distillation of wood and coal.

14. A method according to claim 9, in which the compound is a coal or wood tar selected from light, medium and heavy oils.

15. A method according to claim 9, in which the natural resins are at least one member of the group consisting of pine resins and colophanes.

16. A method according to claim 1, in which the oxygen-liberating compound is ozone.

17. A method according to claim 16 further comprising adding a compound for slowing the decomposition of ozone.

18. A method according to claim 16, in which the aid slowing compound is a member of the group consisting of ether oxide and turpentine.

19. A method according to claim 10, in which the oxygenated compound is an oxygenated salt capable of liberating at least one of chlorine and fluorine at the melting temperature.

20. A method according to claim 1, which comprises, for raw materials containing substantial amounts of copper, adding at least one of calcium and sodium acetate, in amounts equal to 10% of the fluxes contained in the charges.

21. A method according to claim 1, in which the furnace is a cupola, the fuel is coke, and said one of the raw materials is steel.

22. A method according to claim 1, in which for given furnace and charges, plotting the straight lines of tensile strength as a function of carbon equivalent and carbon equivalent as a function of the liquidus temperature; and wherein

\[
\text{carbon equivalent} = \frac{\text{eutectic temperature} - \text{liquidus temperature}}{100} \times 0.90
\]

\[
tensile \text{ strength} = 0.315 \times \text{(liquidus distance)} + B
\]

where B is the basis strength, and further comprising controlling the melting according to the graph corresponding to a given eutectic point.

* * *