Oct. 7, 1958 T. W. CURRY 2,855,336

NODULAR IRON PROCESS OF MANUFACTURE

Filed Feb. 4, 1957 3 Sheets-Sheet 1

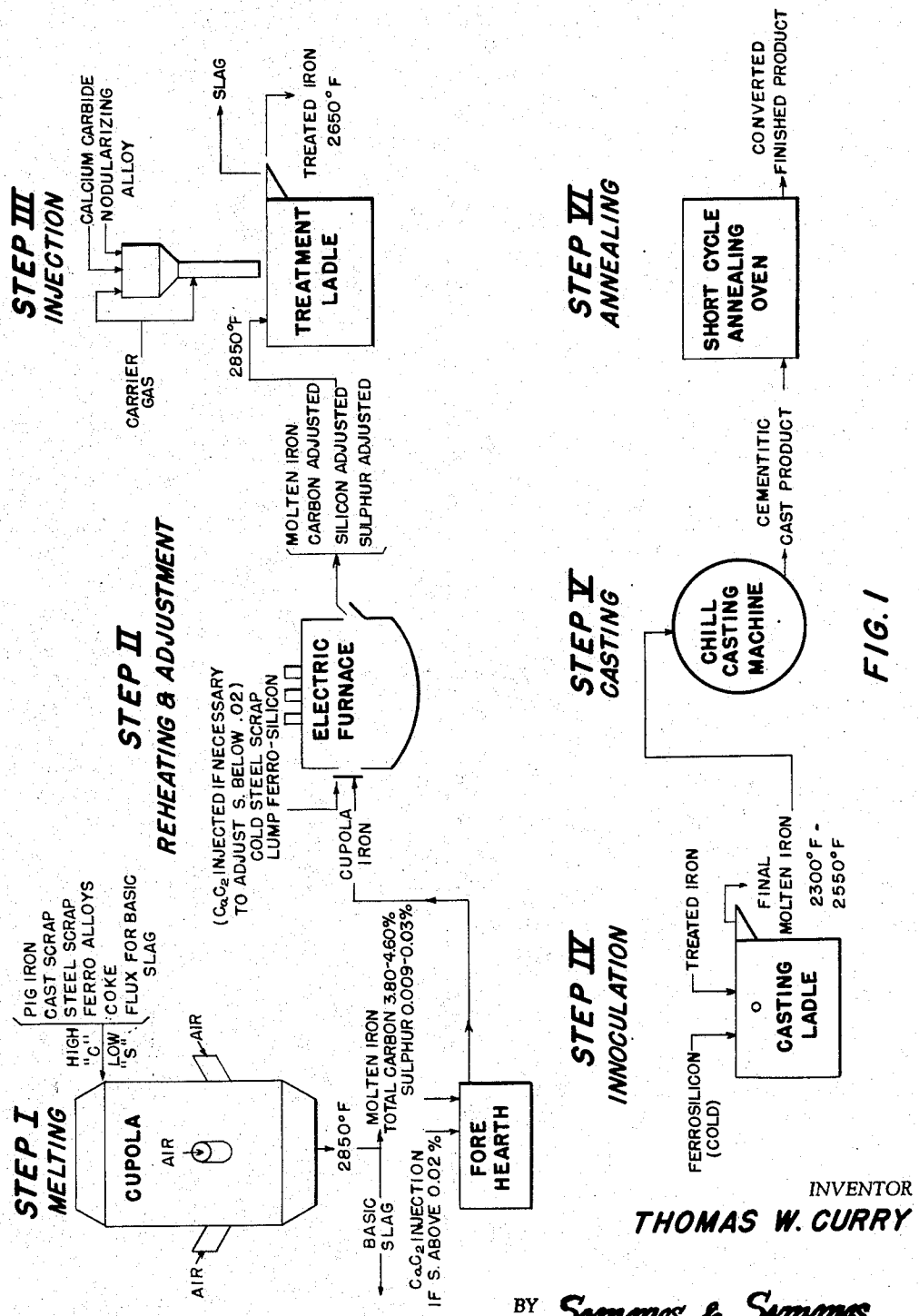


FIG. 1

INVENTOR
THOMAS W. CURRY

BY Symmes & Symmes
ATTORNEYS

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NODULAR IRON PROCESS OF MANUFACTURE

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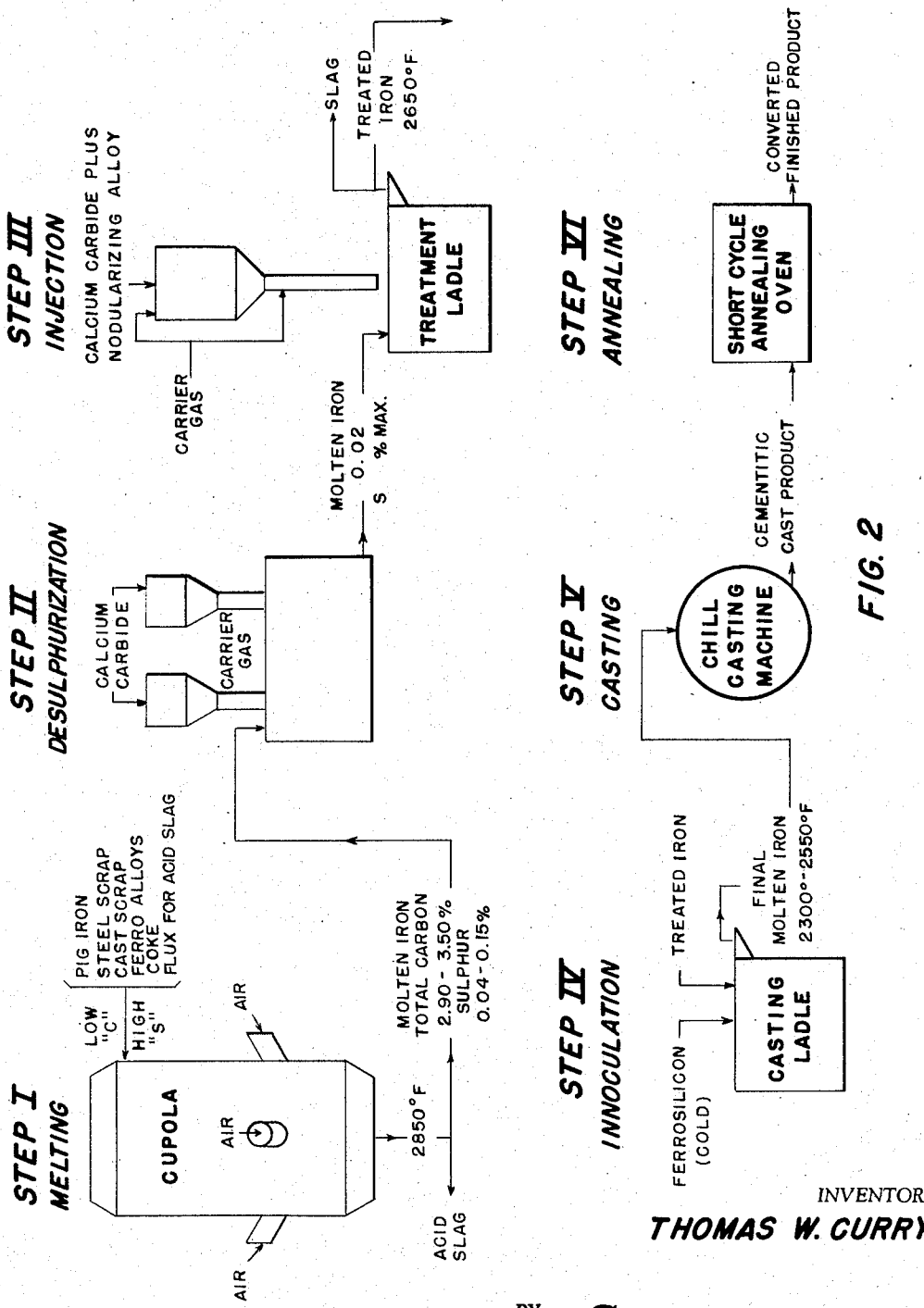


FIG. 2

INVENTOR
THOMAS W. CURRY

BY Sommas & Sommas
ATTORNEYS

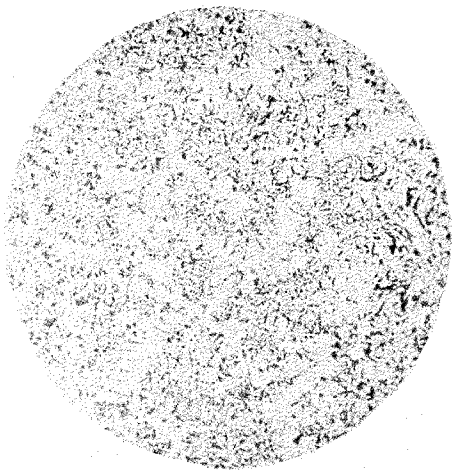
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NODULAR IRON PROCESS OF MANUFACTURE

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FIG. 3

(100X UNETCHED)
REGULAR SUPER DE LAVAUD



TYPICAL SIZE, PATTERN, & DISTRIBUTION OF GRAPHITE. DENDRITIC PATTERN.

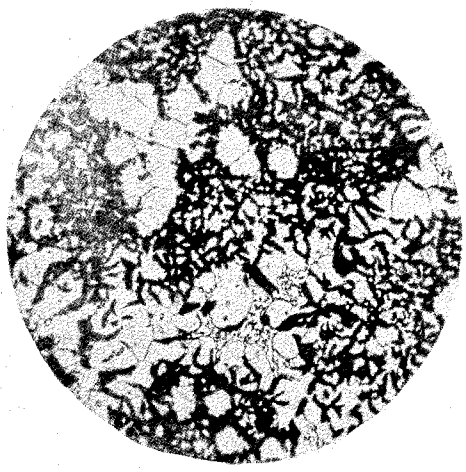
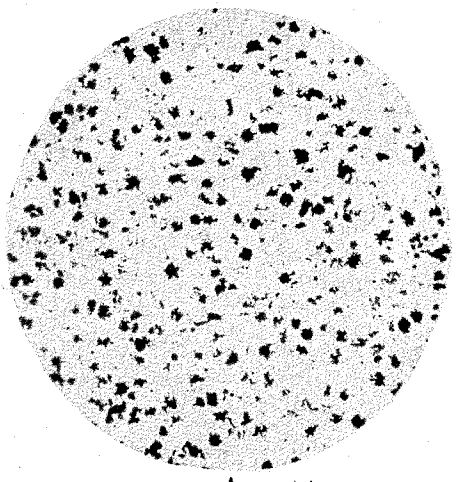


FIG. 5

(500X UNETCHED)
REGULAR SUPER DE LAVAUD

FIG. 4

(100X NITAL ETCHED)
PRESENT CAST IRON PRODUCT



UNIFORM DISTRIBUTION OF FEWER, LARGER GRAPHITE PARTICLES WHICH TEND TO BE SPHERICAL.

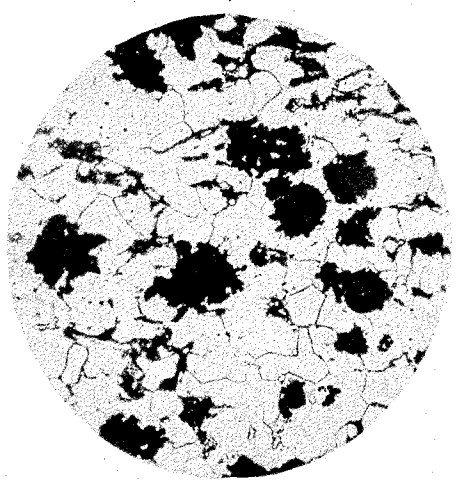


FIG. 6

(500X NITAL ETCHED)
PRESENT CAST IRON PRODUCT

INVENTOR
THOMAS W. CURRY

BY Semmes & Semmes
ATTORNEYS

United States Patent Office 2,855,336 Patented Oct. 7, 1958

2,855,336

NODULAR IRON PROCESS OF MANUFACTURE

Thomas W. Curry, Lynchburg, Va.

Application February 4, 1957, Serial No. 637,957

13 Claims. (Cl. 148—3)

The present invention relates to the production of nodular iron and more especially to an iron which is cementitic upon chill casting and which is thereafter converted to a nodular iron having graphitic nodules, graphitic aggregates and often includes graphitic flakes of short length. The instant application is closely related to my copending patent application Serial No. 549,322, entitled Nodular Cast Iron and Process of Manufacture Thereof, filed November 28, 1955, and patent application Serial No. 638,118, Cast Iron Product of Manufacture, filed February 4, 1957.

The product of the present invention being particularly though not exclusively manufactured for use in De Lavaud pressure pipe, must be competitive in cost with regular grey iron pipe, yet its properties both physical and mechanical must be superior to the present grey iron pipe castings, particularly in impact and shock resistance. The improved physical properties of the nodular iron such as is manufactured hereunder will materially reduce failures previously encountered with the relatively brittle grey iron pressure pipe; breakages being caused in transportation and in ditch installation, earth movement and beam loading in the ground of the length of pipe or breakage in an assembly of pipes as may be caused by surface traffic and improper support of the pipe with fill. Nodular iron of prior manufactures, as for instance that iron having a residual of magnesium above 0.01%, manganese in the range of 0.35% to 0.60%, relatively low copper, chromium and molybdenum and other "tramp" elements, though having excellent physical properties for making pressure pipe, has not as yet been extensively used because of the residual amounts of carbide stabilizing elements and their effect upon the annealing cycle. Available ferrous materials have too high content of these carbide stabilizing elements to make satisfactory nodular iron pipe with the equipment now in use in the De Lavaud process. A very expensive installation for annealing would be required to produce satisfactory pressure pipe having too high a content of carbide stabilizer in the nodular iron. Because the higher content of these stabilizers materially lengthens the annealing cycle and the length of the oven chain must increase as the cycle time increases, it is questionable whether it is mechanically practical to construct the necessary length of oven chain with sufficient strength at the high annealing temperature (1750° F.) to operate under the production requirements of the De Lavaud process. An alternative would be multiple ovens at greater capital expenditure, and if the additional cost were acceptable the higher magnesium content of the conventional method of making ductile iron would prevent annealing in the present short cycle equipment. Today it is believed that to obtain the base metal with a carbide stabilizer content suitable for making nodular iron pressure pipe centrifugally by the De Lavaud process would increase the metal cost per ton of pipe $10.00 over the cost of the metal for conventional grey iron pressure pipe. In prior art developments of

inventors Millis et al., Ihrig, Chrome and Morrogh comparatively great quantities of expensive magnesium and cerium alloys are required in the manufacture of the nodular iron described in their patents. Among the more outstanding patents in this particular field are the following: 2,485,760, Millis et al.; 2,750,284, Ihrig; 2,747,990, Morrogh; 2,692,196, Hulme; and Belgian Patent No. 514,115 of Crockett and Hulme. With respect to the product of Millis and Gagnebin the starting material must be a pig iron with low manganese content or a mixture of steel scrap and pig iron wherein the latter is of at least 50% of the total volume. As to the product of Morrogh, there is required a relatively high residum of cerium therein to overcome the effect of inhibiting elements in production. The product of Ihrig is made by using expensive special pig iron and/or scraps having a relatively low manganese content. Otherwise costly chemical refinements would be required during melting. In Ihrig's process the cold additions made as ladle treatments are in such high amounts that it would be questionable whether his process could be used without some means of reheating during or after inoculation treatment.

The present process yielding the iron product desired calls for the use of an inexpensive steel scrap melt having a relatively low phosphorus content and relatively high content of manganese, namely 0.40 to 0.60%. Moreover, in the manufacture of the particular nodular iron under consideration, it must be adapted to unmodified casting machines and annealing equipment, such as are normally used in industry. The present product is transformed from a cementite on casting to a structure having pearlite, ferrite, graphite, in various shapes including: nodular, flake and aggregate, and a relatively very small amount of cementite, the aggregate being similar to temper carbon aggregate in malleable iron. Thus, the product in question may be called a nodular iron having an absence of a dendritic pattern. The structure of the nodular iron metal produced herein and the shape of the graphite aggregates or nodules are such that the metal has measurable ductility; the mechanical properties of same have been improved by an increase in the ultimate tensile strength, a definite yield point, and measurable elongation. Naturally, ductility improvement accounts for greater resistance of the metal to impact or shock loading.

Nodular iron made by known processes is often of a grade which could not be used commercially in De Lavaud casting machine processes, because of deficiencies in the controls. By "controls" is meant diverse means for eliminating, nullifying or inhibiting the deleterious effect of tramp elements sometimes called subversives or contaminants. Where the controls used in the manufacture of certain nodular irons were such as to give good results, the expense of the control methods made the operations commercially unsatisfactory, considering many of the commercially available starting materials and additives, I have devised the process to yield a satisfactory product wherein all the controls are delicately and accurately employed in such a way as to give universally good results, and where the expense of the combination of steps is such as to be economically competitive with related processes which are employed in the manufacture of grey iron pipe. As indicated, the product of invention is manufactured from steel scrap having low phosphorus content and it is manufactured through utilization of conventional mechanical casting and annealing equipment. The nodular iron above-defined may be obtained through either basic or acid cupola processes, both of which will be defined herein.

In the drawings:

Fig. 1 is a flow sheet of my process, basic cupola;

Fig. 2 is a flow sheet of my process, acid cupola;

Fig. 3 is a photomicrograph at magnification 100 of the iron metal in a conventional super De Lavaud pipe showing the type, size, pattern and distribution of graphite flakes disposed in dendritic pattern;

Fig. 4 is a photomicrograph at magnification 100 of the iron metal in a pipe made by my process. The product shows no tendency to the dendritic pattern of Fig. 3 and the product is iron containing graphite nodules, aggregates and flakes;

Fig. 5 is photomicrograph at magnification 500 of the iron metal in a notal etched specimen taken from conventional super De Lavaud pipe;

Fig. 6 is a photomicrograph at magnification 500 of the iron metal in a nital etched specimen taken from pipe made by my process. Graphitic nodules, flakes and aggregates are shown in a matrix of substantially entirely ferrite, traces of pearlite and cementite being present.

It will be noted that in the De Lavaud process, pipe is centrifugally chill cast in steel molds, the pipe is thereafter annealed, and it is this process which is particularly applicable though not exclusive in the present instance of manufacture. Wall thickness in my nodular iron pipe can be made thinner than in conventional grey iron pressure pipe, and yet my pipe will have the same or greater strength. The ductility of the metal in this pipe has been found considerably greater than such grey iron pipe, and it is less subjected to rupture through shock. The following chart, for example, is a comparison of of the mechanical properties of product pipe made by the De Lavaud steel mold casting process, where super De Lavaud is conventionally produced, and on the other hand a nodular iron pipe of the same diameter and less wall thickness as made by both of my processes, yet similarly cast in a De Lavaud centrifugal steel mold. Both process pipes have been annealed after casting. Note that in the case of the former super De Lavaud the wall thickness was 0.42" and in the present nodular iron pipe the wall thickness was 0.25 to 0.35".

DE LAVAUD PROCESS

Conventional Grey Iron De Lavaud Pipe	8" Diameter Pipe	Present Nodular Iron
18,000–29,000	Bursting Tensile Strength, p. s. i.	50,000–65,000.
40,000–60,000	Modulus of Rupture (Ring), p. s. i.	100,000–120,000.
40,000–60,000	Modulus of Rupture (Strip), p. s. i.	100,000–125,000.
9,000,000–12,000,000	Modulus of Elasticity (Ring), p. s. i.	2,300,000–5,000,000.
8,000,000–12,000,000	Modulus of Elasticity (Strip), p. s. i.	3,400,000–5,000,000.
	Ultimate Tensile Strength, p. s. i.	1" Keel—65,000–80,000.
	Yield Point, p. s. i.	1" Keel—50,000–65,000.
1.20" Bar—28,000–32,000	Ultimate Tensile Strength, p. s. i.	
2,800–3,500	Bursting Pressure, p. s. i.[1]	4,000–5,000.
0.42	Pipe Wall Thickness, inches	0.25–0.35.

[1] Full length of pipe (15'7½").

It will be observed from the above that the present pipe has bursting tensile strength of from 2½ to 3 times that of grey iron pipe which has a wall 20% thicker than the present pipe.

By way of explanation, if the ductility and ultimate strength of a metal is increasing, the modulus of elasticity will increase. In testing all mechanical properties of pipe, as above the Cast Iron Pipe Association uses the secant modulus of elasticity and therefore the lower the value for MB, the better the mechanical properties of the pipe. It is apparent from the above chart that the design of the present nodular iron pipe with its better mechanical properties could be modified, particularly its wall thickness, and thus perform much more satisfactorily than conventional grey iron pipe. This reduction in the wall thickness of the pipe would also naturally result in cost savings.

Prior tests of De Lavaud nodular iron made with processes other than the present have created a casting problem in that the inside and outside surfaces of the pipe were rough and unserviceable. Such expensive pipe had adhering non-metallic inclusions. In these prior art processes, moreover, the fluidity of the metal was such that best results were obtained by increasing the wall thickness quite beyond that required for the standard grey iron pipe. It was also found that nodular iron made by still other processes investigated required a higher pouring temperature at the expense of steel mold life, to produce a useable but not commercially satisfactory surface on the inside and outside of the pipe.

In order to make good nodular iron, for instance, such as can be used in pipe with advantage, it is quite necessary to have flexible controls throughout the process. For example, some of the constituents which must be controlled within desirable limits are percentages of carbon, sulphur, manganese, silicon and phosphorous. In general, the ferrous materials included within the cupola charge comprise cast iron and steel scrap and returns from the nodular pipe casting process. As a practical matter, it is desirable when charging steel scrap to eliminate from the scrap, before melting, armatures of electric motors because of the presence of copper, to eliminate rubber covered steel because of high sulphur content and also to eliminate aluminum, bearing and other non-ferrous metals. Steel scrap containing these inhibiting elements adversely affects the desired formation of spheroidal graphite, for a very small percent of these inhibiting elements in the presence of copper and titanium will upset the process and prevent the formation of graphitic nodules and compacted graphite during annealing. Due to variations in the chemistry of the ferrous charging materials, control treatments at various stages of the process must be undertaken to bring percentages of the desired constituents and other elements within a preferred range. These control treatments will be detailed hereinafter.

PROCESSES

In general my process comprises a melting stage in which the ferrous charging materials are melted in acid or basic cupolas, followed by a calcium carbide injection desulphurization. Sometimes in practice the desulphurization step may be omitted for often available materials and chemical control in basic melting bring the sulphur content below the desirable maximum. In practice this desulphurization step is normally followed by a basic electric furnace re-heating step in which carbon and silicon are adjusted. Of course this third step may be eliminated dependent upon charge and cupola construction. The ensuing step is a treatment step to convert the molten material from typical grey iron characteristics to nodular iron. Following this treatment step is a step of inoculation to make final adjustment of the elements present in the molten mass. From this inoculation step, the materials pass to a chill casting step which is followed by annealing.

Referring to the drawings in Figures 1 and 2, I have diagrammatically shown preferred processes for carrying

out my invention. Alternative processes will be apparent from the following description.

Step I (basic and acid)

In a typical example, Figure 1, there is charged into a basic cupola in the melting step, No. I, steel scrap and cast iron, the latter including returns, from the nodular pipe together with coke and flux to form a basic slag. The following is illustrative:

$$\frac{CaO.MgO.}{SiO_2.Al_2O_3}$$

factor is greater than 1.0. The foregoing comprises the material which is to be charged. All this material is now charged into the cupola and air is injected under pressure for combustion of the coke and to obtain a molten material, the range of temperature being 2850–2950° F. This molten metal is tapped into either a forehearth or ladle, as required. During melting, iron oxide and manganese oxide are formed, the latter being higher in total content than the former named, about 1.5% in the slag. As previously indicated the low sulphur content in the basic cupola method often makes desulphurization unnecessary. A cooling of molten mass occurs and it leaves the forehearth or ladle, at about 2600–2700° F.

A typical charge in the basic cupola of Step I is as follows:

Basic Cupola Metal Charge	Composition of Metal				
	Si, percent	S, percent	Mn, percent	P, percent	TC,[2] percent
(*a*) Metal:					
350# nodular iron pipe return scrap	2.50	0.02	0.45	0.10	3.50
1650# steel scrap	0.20	0.05	0.50	0.05	0.20
Into Basic cupola, charge with	0.60	0.045	0.49	0.059	0.78
Out of cupola spout at 2,850–2,950° F.	[1]0.40	0.05	0.45	0.10	4.20
(*b*) Coke and Flux Per Ton of Metal Charged Into Basic Cupola:					
150# Stone (Mixture of limestone and dolomite).					
350# Coke.					

[1] Silicon loss in cupola is calculated at 33%.
[2] Total carbon.

The percentages of steel scrap and nodular or ductile iron returns shown in the cupola charge may be varied depending upon shop circumstances. Steel scrap would be in the range of 50% to 100% of the charge with nodular iron pipe returns, scrap or cast scrap, making up the balance. The silicon content of the metal out of the cupola would be in the range of from 0.30% to 1.40%.

ACID CUPOLA METAL CHARGE

A typical acid cupola example on the other hand is illustrated in Figure 2. In this process the melt includes 2.90–3.50% total carbon and approximately 0.04–0.15% sulphur. The metal charge includes approximately 85% steel scrap and 15% nodular or ductile iron cast returns. Coke is introduced at from 12 to 18% of the total volume and the flux includes approximately 2% dolomite. The acid slag would have a

$$\frac{CaO.MgO}{Al_2O_3.SO_2}$$

factor of less than 1. The melt leaves the acid cupola at approximately 2850° F. and because of its relatively high sulphur content, must be subjected to desulphurization as in the following step.

Step II (acid only)

In Step II of the drawings of Figure 2, the acid melt is desulphurized in Ladle, or forehearth, by injection of calcium carbide carried in an inert carrier gas such as argon, carbon dioxide or nitrogen. A typical injection to desulphurize acid cupola iron from 0.05% to 0.02% would be as follows: 10 lbs. calcium carbide in 7 cubic feet nitrogen gas injected into a ton of metal according to the following.

Calcium carbide is injected at minus 4.5 pounds per minute with a gas flow rate of minus 100 cubic feet per hour and the injection nozzle is placed at 12–15 inches below the surface of the metal bath; nitrogen gas pressure at the tip of injection tube is at 15 pounds per square inch pressure.

Excesses of calcium carbide or too rapid a feed rate create calcium carbide losses through no metal-wetting of the calcium carbide with a consequent lack of reaction and quite a loss of temperature in the melt. Under the above conditions 10 pounds of injected carbide will remove one pound of sulphur.

The low sulphur content carrying over through Step III, is essential for the successful functioning of subsequent Step IV. As stated, the molten metal as taken from the either basic or acid cupola (Step I) is at a temperature of from 2850–2950° F. The metal from the basic cupola however often requires sulphur and carbon adjustment, hence it must be reheated. If the sulphur content is at 0.02% maximum and the total carbon at from 3.20–3.70% adjustment and reheating may be eliminated.

Step II (basic)

Step II in the basic cupola diagrammatic drawings of Fig. 1 shows an electric furnace where the molten mass is reheated to raise its temperature, and percentages of carbon and silicon are adjusted, as is shown below. The metal charged into the basic electric furnace in Step II has cold steel scrap and 50% ferro-silicon added for the purpose. The temperature of the metal after these Step II additions have been made is in the range of 2500–2600° F., thus it is now raised to 2850–2900° F.

The following is typical of the operating conditions of Step II:

METAL CHARGE TO ELECTRIC FURNACE

1825# cupola metal
175# special steel scrap (cold)
90# 50% FeSi (calculated at 48% Si content and 10% Si loss)

2090#—	Si, percent	S, percent	Mn, percent	P, percent	TC, percent
Into Electric Furnace	2.43	0.02	0.43	0.10	3.60
Out of Electric Furnace	2.19	0.02	0.45	0.10	3.50

The additions made to the molten mass in Step II of Figure 1 can be varied dependent upon the carbon and silicon content of the metal as it is tapped from the ladle (Step I). The cold steep scrap addition may vary from 0% to 20%, and the addition of 50% ferro-silicon will vary between 40 lbs. and 100 lbs. per ton of metal charged.

The sulphur content of the metal tapped from the cupola may be in the range of from 0.01 to 0.05%, however, under normal operating conditions, it is expected that the sulphur content of this metal will not exceed 0.02% maximum. Nevertheless, where the sulphur content of the metal from the cupola is in excess of 0.02%, then desulphurization, Step II, is utilized. Of course, metal with a sulphur content less than 0.02%, as in most basic operations, will normally proceed directly from the cupola to the electric furnace since Step II desulphurization is unnecessary.

The Figure 1 example shows the use of a 50% ferro-silicon alloy addition but the process will work equally well if any commercial grade of ferro-silicon is substituted for the 50% grade. By 50% ferro-silicon is meant 50% silicon in the iron alloy. Commercial grades that

can be used are the commercial grades that run 30% silicon in a ferrous alloy, to 90% silicon therein.

Step III (basic and acid)

In the next step, Step IV (see Figures 1 and 2), the metal is passed to a treatment ladle where nodularizing materials are injected. The carbon and sulphur adjusted metal is tapped from the electric furnace of Step II (Figure 1 or desulphurization forehearth Step II, Figure 2) in amounts suitable for handling in the De Lavaud pipe shop. As each tap of metal is made, an immediate injection of calcium carbide and nodularizing agent is made in the transfer ladle. In the case of the acid cupola process the mechanical mixture is pressure injected simultaneously as the metal is deposited in the ladle. Treatment of the molten iron at 2850–2900° F. as it enters the nodularizing treatment ladle, Step II, changes the composition of the iron so that graphitic nodules will form when annealed (Step VI) if inoculation (Step IV) is made as it is poured into the pipe machine ladle (Step V) as hereinafter explained. The molten mass leaves both nodularizing treatment ladles at about 2650° F.

The following is an example showing a typical Step II:

(a) SIMULTANEOUS INJECTION OF NODULARIZING ALLOY AND CALCIUM CARBIDE PER TON

6.4# alloyed mixture of Mg, Ce, Si alloy
14.4# calcium carbide
10 cubic feet nitrogen carrier gas

	Si	S	Mn	P	TC
Analysis	2.39	0.015	0.45	0.10	3.50

To obtain residual magnesium in the range of 0.005 to 0.01% its presence in the nodular iron should be in excess of cerium by a minimum of four times, to yield the best results with white iron pipe, through the nodular process herein. The nodularizing alloy itself contains a greater excess of magnesium, of course. Pure magnesium metal in this treatment step is unsatisfactory because it promotes a more stable cementite and inhibits transformation, a factor which would make the process ill-adapted to the short cycle annealing (Step VI) for which the process is designed.

The silicon content in Step IV shown in the example can be in the range of 2.00% to 2.70%; the total carbon content could be in the range of 3.30 to 3.70%; sulphur is at 0.02% max. and the process would be satisfactory.

The nodularizing alloy which is injected simultaneously with the calcium carbide can be a magnesium-cerium-silicon ferro alloy. A typical injection as indicated in the figures given above comprises a simultaneous injection of 14.4 lb./T calcium carbide and 6.4 lb./T of magnesium-cerium-silicon ferro alloy in 10 cu. ft. of nitrogen carrier gas. This is equivalent to 0.025% magnesium. It will be appreciated that in recovering such critical quantities of residual magnesium (0.005–0.01%) in the metal under these conditions, a control against consistent magnesium oxidation must be effected during injection. For this reason, I have selected the above control ratio of calcium carbide to magnesium, great care being taken to inject the alloy and carbide at precisely the same moment. A typical nodularizing alloy is as follows: Mg 8.5%, Ce 0.5%, Si 45%, Al 1.25% with the balance iron.

I have found that the residual cerium content of the nodular iron with the above-mentioned alloy is sufficient to develop the graphite structure necessary for the improved physical properties of the metal and the improved mechanical properties of the pipe. The amount of residual cerium in the metal is so small, however, that its presence can only be shown by the spectrograph and not correctly analyzed quantitatively.

Aside from the iron-silicon-cerium-magnesium group these alloys have been found suitable:

(*a*) Mg 15.0—20.0%, Ni 85.0—80.0%; and
(*b*) Mg 12.0—15.0%, Si 30.0%, Ni 40.0—50.0%.

Copper and nickel retard second stage annealing and thus when these copper and nickel alloys are used in either acid or basic process, I add Mischmetal having 50% cerium added to offset the effect of inhibiting agents present.

In this nodularization we recover from between 0.005% to 0.009% magnesium in the annealed product. Otherwise stated, there is a 25% recovery of residual magnesium considering the amount of magnesium alloy added. Residual magnesium in excess of 0.01% does not produce the structure desired in the pipe with the annealing cycle employed in the process. Residual magnesium from 0.005–0.009% will develop the desired properties. It has been found that the higher the magnesium content of the alloy, the more erratic is the control of residual magnesium in the nodular iron; moreover a residual of greater than 0.01% adversely affects the conventional annealing cycle that is so important in the manufacture of inexpensive castings.

It is calculated that an addition of cerium, a nodularizing alloy or Mischmetal or both to place cerium residual is estimated in the range of 0.001 to 0.003%.

In the present process the preferred nodularizing magnesium alloy is an iron-silicon-cerium alloy.

Many magnesium-cerium-silicon ferro alloys are susceptible of satisfactory employment in my process. Economics, of course, will be affected with major changes in the cerium and magnesium contents of these nodularizing alloys. In general, alloys, the composition of which will fall within the limits expressed below in percentages by weight, may be used:

Percent Ce	Percent Si	Percent Mg	Percent Ca	Percent Al
0.38–0.8	40.0–55	5.0–20–0	0–3.5	0.5–3.0

Metal melted in a cupola is known to have oxides which some investigators have described as "slimes." These oxides are determimental to ultimate physical properties of the iron and have an effect upon its structure formation. It is also known that elemental nitrogen and/or nitrogen compounds are detrimental to the physical properties of steel and grey iron. In this connection, work has been done to show likewise that hydrogen, generated in the 5000° F. arc of the indirect-arc electric furnace has a detrimental effect upon the physical properties of grey iron.

In Step III of the process where calcium carbide is injected into the metal with nitrogen gas (N2), I believe that oxide slimes, nitrogen (N), nitrogen compounds and hydrogen may be removed from the metal and this removal has a desirable effect upon the annealing characteristics of the nodular iron. This concept is supported by recent efforts in Germany in which the melt is flushed with nitrogen gas to remove such undesirable nitrogen (N) and nitrogen compounds.

It is to be understood that whereas there is shown but one treatment station for injection at Step III and in the forehearth or transfer ladle of Step I, a plurality of injections may be used, for in practice the greater the number of injectors, the greater the efficiency in operation.

After the metal has been treated by the injection of the calcium carbide and the nodularizing agent in the nodularizing treatment ladle, it is transferred to the De Lavaud pipe machine floor. Generally, the metal is held less than ten minutes in the nodularizing treatment ladle.

Step IV

Step IV, which takes place when the metal is transferred to the pipe machine ladle is one in which a ferrosilicon addition is made to raise the silicon content and inoculate the molten mass immediately preceding casting (Step V), to promote formation of a structure having

the best mechanical properties after annealing (Step VI). The following is typical of this inoculation treatment:

Ferro-Silicon Addition at De Lavaud Machine Ladle [1]	Composition of Metal				
	Si	S	Mn	P	TC
5# 75% grade ferro-silicon alloy for ladle addition, per Ton. Analysis	2.54	0.015	0.45	0.10	3.50

[1] At 75% Si and 80% recovery, this addition adds 0.15% Si to the metal.

This final addition of 75% grade ferro-silicon alloy (75% Silicon) can be changed to any commercial grade or even pure silicon metal; the actual silicon addition may vary from 0.15% to 0.60% of the total molten mass. It is to be noted, however, that the addition of this silicon (Step IV), over that added during nodularization (Step II) is 0.15%.

The final molten iron is now ready to pass into the DeLavaud machine for casting and has a temperature of 2300–2550° F.

Step V

In Step V, Figures I and II, the pipes are chill cast in the De Lavaud machine, yielding cementite. The process of casting an iron on a chill refines the grain size, and all other factors remaining equal, the smaller the grain size of the white iron, the more rapidly the desired transformation from cementite to pearlite and ferrite takes place during annealing. To illustrate the transformation that takes place a 0.008% residual Mg nodular iron, chilled cast and annealed, would have the same physical properties as a sand cast 0.04 Mg nodular iron. The process of very rapidly cooling the nodular iron pipe metal through its upper critical temperature range (1650–1750°) and subsequently annealing would, in a sense, be equal to adding five times more Mg to an iron made under the known processes wherein the product is normally sand cast. Stated another way, if one does not chill cast, he must add greater amounts of Mg to obtain the desired product. If one does chill cast, on the other hand, less amounts of Mg are required to obtain the desired product having comparatively smaller nodules, and aggregates and flakes as shown, and the residual Mg content must be controlled at less than 0.01% or additional annealing ovens or longer annealing ovens will be necessary.

Step VI

In Step VI, the cementitic cast pipe are charged into the short cycle annealing oven. In annealing I seek to effect structural changes in the metal, e. g., cementite transformation to pearlite and graphite; pearlite to ferrite and graphite. To attain the desired transformation annealing must be carried out within a critical temperature range. In chill casting I have formed cementite by rapid cooling of the cast iron through the range of 1650° F. to 1750° F.; now on transfer from the chill casting machine heat is lost. Hence upon annealing the cementitic product is heat-treated first in the zone of 1650–1750° F. for cementite transformation and secondly in the critical range of 1250 to 1450° F. for pearlite transformation. As stated the transformations ultimately yield the ferrite with graphitic nodules, flakes and aggregates. My annealing cycle is therefore designed so that the nodular iron is raised to 1750° F. and held at this temperature to transform the cementite to pearlite, ferrite, and free graphite. In the case of nodular iron pipe metal, the higher the temperature of the first-stage anneal the more rapidly the transformation of cementite occurs. Beyond 1750° F., excessive oxidation and out-of-roundness is encountered and the more difficult it would be mechanically to drop the temperature of the pipe to the second-stage annealing zone (1250–1450° F.) where pearlite is transformed to ferrite and free graphite.

Since this is a process in which metallurgical control features are of paramount importance, I will now describe in detail the controls used.

CARBON CONTROL

The total carbon content of the metal tapped from the basic cupola will be in the range of 4.00 to 4.60% and can be adjusted downward to the desired level by an addition of cold steel scrap in the electric furnace. There are possibilities to reduce the carbon content of the metal as tapped from the basic cupola, by changing the composition of the basic slag and thereby reducing the amount of cold steel scrap to be added in the electric furnace. If, in the process of refining the basic slag of the cupola for the most economical electric furnace operation, the total carbon content is lowered below the desired level, carbon could be added to the bath by the injection process.

CONTROL OF MANGANESE

The manganese control of our raw materials is somewhat fixed so that the melt from the basic cupola will contain manganese in the range of 0.35% to 0.55%. A nodular iron containing manganese in this range will anneal satisfactorily in our annealing oven with the short annealing cycle. There is a possibility, however, of some manganese steel scrap or other scrap materials containing manganese higher than the indicated desired level, entering into the cupola mixture. The manganese content, in these few instances, may be adjusted to the desired level by an addition in Step II (Figure 1) in the electric furnace of converter metal which would be on hand to take care of this adjustment, or the use of a special low-manganese pig iron purchased from an outside source.

The converter metal referred to is one low in manganese, silicon and carbon. The use of the converter metal takes the manganese percentage down and silicon and carbon can be added if necessary to obtain the desired percentage of these elements.

CONTROL OF SILICON

It is to be expected in this process, that the silicon content of the metal in the electric furnace would always be on the low side of the desired range. Silicon can be added in the electric furnace by an addition of any of the commercial grades of ferro-silicon, or by the injection of silicon metal.

In the extreme case of having the silicon content too high, pig converter metal or steel scrap could be added. These materials would, in lowering the silicon content, lower the carbon content and carbon may be injected to raise the level to the desired range.

CONTROL OF PHOSPHORUS

The phosphorus content of the nodular iron pipe should not exceed 0.12%, for best physical properties. If, in the use of high percentages of cast scrap in the cupola charge, the phosphous content is above the desired level, steel scrap may be added to the electric furnace to adjust the phosphorus content to 0.12% maximum. The steel scrap addition will lower the total carbon content and the carbon can be adjusted by injection.

In connection with the process and product made by this process, a comparison between regular super De Lavaud pipe, centrifugally cast in steel molds, and the thin-wall nodular iron pipe made by my process described in this application is desirable. The regular grey iron super De Lavaud pipe is one with a dense close grain metal which is very suitable for ordinary applications but the tests that follow will show that it is in practically every way inferior to the product made by my process. A comparison between the pipes from the point of view of photomicrographs will indicate radical differences in the structure of the metal. Pipe made by my process have physical properties which are ample to justify the thin wall thickness I may employ, for I can have a con-

siderably thinner wall pipe with greater strength than with the regular super De Lavaud pipe.

CHEMICAL COMPOSITION

6" Pipe	Regular Super De Lavaud	New Process
Lab. No	159,767	161,496
Percent Si	1.78	2.59
Percent S	0.065	0.018
Percent Mn	0.52	0.54
Percent P	0.38	0.10
Percent T. C	3.74	3.53
Percent Mg		0.006

PHYSICAL PROPERTIES

[Talbot strip tests]

6" Pipe	Regular Super De Lavaud	New Process
Thickness, inches	.435	.250
Deflection, inches	.130	.790
Lb. Load	635	670
M/R	48,300	107,100
M/E	9,400,000	5,020,000
B-Rockwell	84-81-73	87-87-77

1. Thickness is actual thickness of pipe wall.
2. Deflection is distance strip bent before breaking.
3. Lbs. load is actual transverse load required to break a ½" wide x 12" long strip machined from wall of pipe on 10" centers.
4. M/E is Modulus of Rupture which is a measure of strength. Pipe specifications require that this be in excess of 40,000 p. s. i.
5. M/R is Modulus of Elasticity which is in this test a measure of stiffness or resistance to bending. Pipe specifications require that this not exceed 12,000,000 p. s. i.
6. B-Rockwell is measure of hardness across pipe wall. Pipe specifications require that this not exceed 95.

RING CRUSHING TESTS

[Tests made on 3" length rings by standard procedure]

6" Pipe	Regular Super De Lavaud	New Process
Lbs. Load	6,280	3,860
Deflection, inches	.130	.665
Thickness, inches	.418	.246
M/R	64,300	135,300

BURSTING TESTS

[Tests made on 15' 7½" lengths of plain end pipe. Pipe burst by applying hydrostatic pressure at a slow steady rate]

	Regular Super De Lavaud	New Process
Minimum Thickness, inches	.368	.211
Average Thickness, inches	.370	.215
Bursting Pressure, p. s. i	3,625	3,200
Bursting Tensile, p. s. i	29,900	63,500

SUMMARY OF PHYSICAL PROPERTIES

	Requirements	Actual Results	
		Regular Super De Lavaud	New Process
Strip M/R, min	40,000	58,300	107,100
Strip M/E, max	12,000,000	9,400,000	5,020,000
Ring M/R, min	40,000	64,300	135,300
Bursting Tensile, min	18,000	29,900	63,500

Referring to the drawings, Figure 3 is a photomicrograph of the metallic structure in a regular super De Lavaud pipe 6 inches in diameter cast to 0.38 inch wall thickness and magnification 100 diameters. The metal here is unetched. This photomicrograph, Figure 3, shows typical size, pattern and distribution of graphite found in the wall of a super De Lavaud pipe. The flakes of graphite are numerous and extremely small and are arranged in what is known as a dendritic pattern.

Figure 4 is a photomicrograph of the metallic structure of an iron pipe made by my process. The pipe is 6 inches in diameter with a wall thickness of 0.25 inch. Here also the magnification is 100 diameters and the metallic surface is unetched. The graphite particles throughout the wall of the new process pipe are larger and far less numerous than in Figure 3 and generally tend to be somewhat spherical in shape. They are quite uniform in distribution and show no tendency to the dendritic pattern shown in photomicrograph Figure 3.

Referring to Figure 5 I have shown a photomicrograph of the metallic structure of a regular super De Lavaud pipe of 6 inches diameter cast to 0.38 inch wall thickness; magnification is 500 diameters and the pipe has been etched with a 2% solution of nitric acid and alcohol. This photomicrograph is a portion of the field shown in photomicrograph Figure 3 after etching and at a higher magnification. The structure consists of a fine graphite network in a matrix of ferrite. A small amount of iron phosphide is visible in the lower portion of the field.

In comparison, see Figure 6 which is a photomicrograph of a 6 inch diameter iron pipe made by my process cast to 0.25 inch wall thickness. The surface of the metal has been etched in the customary manner and the magnification is 500 diameters. This is a portion of the field shown in photomicrograph Figure 4 after etching and at a higher magnification. The structure consists of compact particles of graphite in a matrix of practically all ferrite. Traces of pearlite and cementite are present.

In conclusion, whereas the iron melted in the basic cupola method had a high carbon and low sulphur content, in the acid cupola method, the iron melted has a low carbon and high sulphur content. In the acid process, it is proposed to eliminate reheating the melt. It will be recalled that, in addition to the requirement for heating as in Step II (basic cupola method) it was necessary to adjust, by a steel scrap and ferro-silicon addition, the carbon and silicon contents after desulphurization. Now by variation of the charge in the acid cupola, such adjustments are unnecessary. As an elucidation of the first step of this acid cupola method, attention is directed to the following chart in which the precharges of elements of the melt as shown, said elements being tapped from the cupola.

Acid Cupola Metal Charge	Composition of Metal				
	Percent Si	Percent S	Percent Mn	Percent P	Percent TC
(a) Metal:					
500# Steel Scrap	0.20	0.05	0.50	0.05	0.20
1430# Cupola Iron	0.50	0.02	0.50	0.08	4.20
77# Lump, 50% Fe Silicon	48.0				
Into Acid cupola charge	2.28		0.50		3.03
Out of acid cupola	2.00	0.10	0.45	0.10	3.45
(b) Coke and flux per ton of metal charged into acid cupola: 300# Coke. 50# Silicon Rock. 25# Dolomite.					

Sulphur in the iron tapped from the acid cupola would be reduced in desulphurization (Step I) from 0.10 to 0.02% by an injection of 20# of calcium carbide per ton of metal. In acid cupola melting practice there is a gain in sulphur, phosphorous, total carbon being as shown in the chart. Through this process, I usually obtain the following percentages of elements in metal tapped from the acid cupola; 2% silicon; 0.45% manganese; 3.40–3.50% total carbon; 0.10% phosphorus; 0.07 to 0.11% sulphur.

It will be apparent from the foregoing that my processes have produced a valuable iron at reasonable cost

with control factors which permit of uniform results in the final product.

I desire that my invention be limited solely by the scope of the appended claims and the showing of the prior art.

1. A process of producing an annealed cast iron of improved ductility which comprises the steps of forming a molten iron containing a low phosphorus and normal manganese content, adjusting the carbon, silicon and sulphur content thereof to form a composition which would yield a grey iron in as-cast condition, injecting said molten iron with an intimate admixture of calcium carbide and a magnesium-cerium bearing nodularizing agent to form a composition which would yield a grey iron containing free graphite in nodular form in as-cast condition, chill casting the molten composition to produce a white iron in which substantially all of the carbon remains in combined form, reheating the cast iron to a temperature of from 1650°–1750° F. to convert the iron matrix from cementite to pearlite and lowering the temperature gradually to 1250° F. to transform the pearlite to ferrite and to release the combined carbon as a mixture of nodules, flakes and aggregates.

2. A process of producing an annealed cast iron of improved ductility which comprises the steps of forming a molten iron containing a low phosphorous and normal manganese content, adjusting the carbon, silicon and sulphur content thereof to form a composition which would yield a grey iron in as-cast condition, injecting said molten iron with an intimate admixture of calcium carbide and a magnesium-cerium bearing nodularizing agent in such quantities as to form a composition containing residual magnesium in an amount less than 0.01% by weight and residual cerium in an amount so slight as to be determinable only qualitatively which would yield a grey iron containing free graphite in nodular form in as-cast condition, chill casting the molten composition to produce a white iron in which substantially all of the carbon remains in combined form, reheating the cast iron to a temperature of from 1650°–1750° F. to convert the iron matrix from cementite to pearlite and lowering the temperature gradually to 1250° F. to transform the pearlite to ferrite and to release the combined carbon as a mixture of nodules, flakes and aggregates.

3. A process of producing an annealed cast iron of improved ductility which comprises the steps of forming a molten iron containing a low phosphorus and normal manganese content, adjusting the sulphur content of the molten iron to a maximum of 0.02% by weight by the injection therein of calcium carbide, adjusting by selective additions of steel scrap and ferro-silicon the carbon content of the molten iron to constitute approximately 4% by weight and the silicon content of the molten iron to constitute approximately 1.75% by weight of the composition which would yield a grey iron in as-cast condition, injecting said molten iron with an intimate admixture of calcium carbide and a magnesium-cerium bearing nodularizing agent in such quantities as to form a composition containing residual magnesium in an amount less than 0.01% by weight and residual cerium in an amount so slight as to be determinable only qualitatively which would yield a grey iron containing free graphite in nodular form in as-cast condition, chill casting the molten composition to produce a white iron in which substantially all of the carbon remains in combined form, reheating the cast iron to a temperature of from 1650°–1750° F. to convert the iron matrix from cementite to pearlite with a partial release of the combined carbon and lowering the temperature gradually to 1250° F. to transform the pearlite to ferrite with a further release of combined carbon, the freed graphite appearing as a mixture of nodules, flakes and aggregates.

4. A process as defined in claim 3 in which the molten iron is inoculated by an addition of ferro-silicon alloy immediately preceding casting thereof.

5. A process of producing an annealed cast iron of improved ductility which comprises the steps of forming a molten iron with a phosphorus content below 0.12% by weight and a manganese content in the range of from 0.35% to 0.55% by weight, adjusting the sulphur content of the molten iron to a maximum of 0.02% by weight by the injection therein of calcium carbide, adjusting by selective additions of steel scrap and ferro-silicon alloy the carbon content of the molten iron to constitute approximately 4% by weight and the silicon content of the molten iron to constitute approximately 2.75% by weight of the composition which would yield a grey iron in as-cast condition, injecting said molten iron with an intimate admixture of calcium carbide and a magnesium-cerium bearing nodularizing agent in such quantities as to form a composition containing residual magnesium in an amount less than 0.01% by weight and residual cerium in an amount so slight as to be determinable only qualitatively which composition would yield a grey iron containing free graphite in nodular form in as-cast condition, chill casting the molten composition to produce a white iron in which substantially all of the carbon remains in combined form, reheating the cast iron to a temperature of from 1650°–1750° F. to convert the iron matrix from cementite to pearlite with a partial release of the combined carbon and lowering the temperature gradually to 1250° F. to transform the pearlite to ferrite with a further release of combined carbon, the freed graphite appearing as a mixture of nodules, flakes and aggregates.

6. A process as defined in claim 5 in which the molten iron is inoculated by an addition of ferro-silicon alloy immediately preceding casting thereof.

7. A process as defined in claim 5 in which the nodularizing agent is an alloy of magnesium, cerium and silicon and the ratio of magnesium to cerium therein is at least 4 to 1.

8. A process as defined in claim 5 in which the molten metal is at a temperature of from 2650–2700° F. at the start of the calcium carbide-nodularizing agent injection.

9. A process as defined in claim 1 in which the nodularizing agent injection is performed in the absence of oxygen, primarily to desulphurize the metal and secondarily to remove influential oxides, nitrides, and elemental nitrogen from the metal.

10. The process according to claim 9 in which the injection is performed with an inert gas as a carrier for the nodularizing agent.

11. The process according to claim 10 in which the gas is nitrogen.

12. The process according to claim 10 in which the gas is carbon dioxide.

13. The process according to claim 10 in which the gas is argon.

References Cited in the file of this patent

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OTHER REFERENCES

Transactions, American Foundrymen's Society, vol. 58, pages 310 and 311. Published in 1950 by the foregoing Society.

UNITED STATES PATENT OFFICE

Certificate of Correction

Patent No. 2,855,336 October 7, 1958

Thomas W. Curry

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the drawings, Sheet 3, Fig. 4, for "(100x nital etched)" read —(100x unetched)—; Fig. 5, for "(500x unetched)" read —(500x nital etched)—; column 2, line 13, for "residum" read —residuum—; line 56, for "additives," read —additives—; column 3, line 12, for "notal" read —nital—; line 65, for "MB" read —ME (modulus of elasticity)—; column 4, line 16, for "phosphorous" read —phosphorus—; column 5, lines 65 and 66, for

$$\frac{CaO.MgO}{Al_2O_3.SO_2} \quad \text{read} \quad \frac{CaO.MgO}{Al_2O_3.SiO_2}$$

column 6, line 66, for "Step II" read —Step I—; column 7, line 5, for "Step IV" read —Step III—; line 17, for "Step II" read —Step III—; line 20, strike out "(Step V)"; line 23, for "Step II" read —Step III—; line 44, for "Step IV" read —Step III—; column 9, line 18, for "II)" read —III)—; column 10, line 57, for "phosphous" read —phosphorus—; column 11, line 30, item 4, for "M/E" read —M/R—; line 31, item 5, for "M/R" read —M/E—; column 12, line 68, and column 13, line 27, for "phosphorous", each occurrence, read —phosphorus—.

Signed and sealed this 31st day of March 1959.

[SEAL]

Attest:
KARL H. AXLINE,
Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.