The invention relates to an improved method for producing ductile cast iron and to a new agent for use in such method. Ductile cast iron may be defined as cast iron which exhibits plastic strain in tension in an amount equivalent to at least 1% permanent elongation before fracture. Ductile cast iron may be further characterized as cast iron containing an effective amount of graphite of the type that appears as spheroids in the as-cast condition. Such iron, due to its ductility and other desirable physical properties, constitutes a valuable material in industry and may be employed in some uses hitherto limited to steels.

It is known that cast iron having a spheroidal or nodular structure may be prepared from a molten bath of cast iron of specified composition and under controlled conditions by incorporation into the bath additions of such metals as cerium, titanium, beryllium, lithium, and magnesium. The prior art processes, however, have certain inherent difficulties and limitations. For example, additions of cerium appear to be effective in the production of a nodular structure only when added to hypereutectic cast irons of extremely low sulphur content. Additions of elemental magnesium, however, appear to produce a nodular structure in both hypo and hypereutectic cast irons. Despite this broader range of applicability the addition of magnesium to cast iron results in certain serious operational difficulties. When elemental magnesium is added to molten cast iron there is a violent, almost explosive, reaction. The violence resulting from the addition of magnesium not only constitutes a major hazard to such an operation but, due to expelled cast iron and magnesium, renders reproducibility of a uniform product by such an addition uncertain, if not substantially impossible. The addition of elemental magnesium to cast iron for the production of a nodular structure is commercially unattractive for another and equally serious operational difficulty. Although the introduction of magnesium appears to be effective in converting both hypo and hypereutectic cast iron to the desired nodular structure, the effect is of extremely short duration. This fading effect of the magnesium addition necessitates the immediate casting of the iron after the magnesium addition and subsequent inoculation. If casting is delayed even for a matter of minutes the effect of the addition is lost and a product is obtained which is substantially the same as that which would be obtained if no magnesium had been added. Since the fading effect of the magnesium addition is progressive, there is again the difficulty of reproducibility of uniform properties in the cast material. A further disadvantage to the use of magnesium as an addition agent for the purposes mentioned is the tendency of this element to produce white iron thus rendering the treated material more sensitive to the formation of chill.

Prior art workers have attempted to ameliorate these difficulties by alloying the magnesium with other metals, for example nickel and copper, prior to its introduction into the molten cast iron. Such alloys when the concentration of magnesium is below 30%, preferably even lower, are less violent when introduced into the molten bath. Alloying the magnesium with other metals, however, has not resulted in eliminating the objectionable fading effect and accordingly such alloys are still unattractive in commercial operations. Furthermore, when nickel or copper is alloyed with magnesium to act as a buffer metal in reducing the violence of the magnesium addition, the buffer metal is necessarily incorporated in the cast iron. This often may be undesirable particularly when the cast iron is subsequently used as scrap in the preparation of other materials. Since neither nickel nor copper is oxidizable in molten iron these metals unavoidably appear as contaminants in the new material in which the scrap from previous melts is utilized.

It is a primary object of the present invention to provide an improved method for the production of ductile cast iron which method greatly extends the interval of time for which the treated cast iron may be held prior to casting thereby overcoming the objectionable fading effect hereinbefore described.

A further object is to provide a unique agent for use in such method which agent is suitable for the production of ductile cast iron from both hypo and hypereutectic cast irons and which is free from the hazards associated with the use of some of the prior art materials.

A still further object is to provide an agent which when employed in the method of the invention will decrease the tendency of chill formation in the treated iron.

The manner in which these and other objects of the invention are attained will be apparent as this specification proceeds.

In the work leading to the present invention it was discovered that additions of zirconium to cast iron resulted in the production of nodular graphite. One limitation on the use of zirconium as an addition agent to cast iron is the difficulty of achieving solution of the zirconium
In cast iron and in retaining significant amounts of residual zirconium in the final treated product. It was discovered that elemental magnesium was an excellent agent for increasing the recovery of zirconium when the elemental magnesium and zirconium material were comminuted and incorporated as a mechanical mixture into briquette form. It was found as a most surprising result that molten cast iron treated with briquettes containing a mechanical mixture of zirconium and elemental magnesium and innoculated in the customary manner could be held for appreciably lengthy periods of time with no adverse or fading effect and that the last casting poured had substantially the same excellent strength, ductility and other physical properties as the first casting poured.

According to the invention the new agent comprises a mechanical mixture of comminuted elemental magnesium and comminuted zirconium-bearing material in a suitably bonded condition. Bonding or briquetting may be done in any well known manner such as by bonding with a 10% solution of sodium hydroxide in an amount sufficient to obtain a strong pellet. In the bonded material the ratio of the zirconium content to the elemental magnesium content should not be more than 3 and preferably about 1, and the ratio of the elemental magnesium content to the zirconium content should not be more than 3 and preferably about 1. The zirconium may be added to the pellet as a comminuted zirconium-bearing material such as comminuted zirconium-silicon, or other zirconium-bearing material provided the composition is such that the final mechanical mixture is within the required composition ranges. Without regard to binder material, the composition of the pelletted mechanical mixture of comminuted zirconium-bearing material and comminuted elemental magnesium should be within the following ranges:

<table>
<thead>
<tr>
<th>Bonded</th>
<th>Preferred</th>
</tr>
</thead>
<tbody>
<tr>
<td>Per cent</td>
<td>Per cent</td>
</tr>
<tr>
<td>Zirconium</td>
<td>10-30</td>
</tr>
<tr>
<td>Silicon</td>
<td>1-45</td>
</tr>
<tr>
<td>Iron</td>
<td>5-45</td>
</tr>
<tr>
<td>Magnesium</td>
<td>10-30</td>
</tr>
</tbody>
</table>

It is understood that the composition may also include such incidental impurities as may be present in the zirconium-bearing material and commercial scrap magnesium metal.

In preparing the materials for the mechanical mixture of the invention, the comminuted zirconium-bearing material should not exceed about 20 mesh (0.033 inch screen openings) maximum particle size and the comminuted elemental magnesium preferably should not exceed about 30 mesh (0.0234 inch screen openings) maximum particle size.

In order to demonstrate the effectiveness of the method of the invention under actual foundry conditions, a series of test castings were prepared from a cupola melted all pig iron charge treated as below.

750 pounds of the cupola melted charge was collected into a bull ladle and treated with 0.50% zirconium and 0.50% magnesium in the form of a briquetted mechanical mixture of comminuted zirconium-silicon alloy and comminuted elemental magnesium. The nominal analysis of the briquettes was 27% zirconium, 27% magnesium, 35% silicon, the remainder iron. The briquettes were placed in paper bags and added to the ladle after the bottom of the ladle was covered with molten cast iron. There was considerable bubbling action in the molten metal upon the addition of the briquettes which served to agitate the bath and aid in uniformly distributing the addition agent throughout the entire metal mass. The action was insufficient to evert any metal from the ladle. The treated iron was poured from the 750-pound ladle into 40-pound size ladles and innoculated with 0.40% silicon as a silicon-bearing iron alloy containing about 65% silicon. In order to demonstrate the effect of holding time on the properties of the final product, the test castings were poured over an eight minute interval. There was no decrease in mechanical properties during the time interval investigated, thus demonstrating the absence of the objectionable fading effect heretofore encountered in the production of ductile cast iron by prior art processes. Data obtained from tensile specimens cut from the keel block castings, together with the time at which the cast iron was poured after the zirconium-magnesium treatment, are shown in the table below. In the table casting time after treatment with the briquettes of the invention is given in minutes and seconds. Y. S. 1000 p. s. i. means yield strength in thousand pounds per square inch. T. S. 1000 p. s. i. means tensile strength in thousand pounds per square inch. Percent elong. in 2 in. means percentage elongation in two inches. Percent Red. area means percentage reduction in area at the tensile fracture.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Percentage Composition</th>
<th>Casting Time After Treatment</th>
<th>Y. S. 1000 p. s. i.</th>
<th>T. S. 1000 p. s. i.</th>
<th>Per Cent Elong. in 2 in.</th>
<th>Per Cent Red. of Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.20 3.14 0.033 0.74 0.11 0.034</td>
<td>49 32 95</td>
<td>55.5 75.8 5.0</td>
<td>3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.48 3.06 0.036 0.72 0.034</td>
<td>49 32 95</td>
<td>55.5 75.8 5.0</td>
<td>3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.48 3.48 0.047 0.094 0.090</td>
<td>6 10 90</td>
<td>75.8 75.8 4.0</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3.48 3.48 0.047 0.094 0.090</td>
<td>6 10 90</td>
<td>75.8 75.8 4.0</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3.48 3.48 0.047 0.094 0.090</td>
<td>6 10 90</td>
<td>75.8 75.8 4.0</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It will be noted from the table that the tensile and yield strengths, percentage elongation and reduction in area of the test specimens are extremely uniform. In fact the specimen taken from test No. 5, poured nearly eight minutes after the briquette treatment, had somewhat better ductility than the specimen taken from the casting of test No. 1 poured fully three minutes earlier. The test data clearly establishes that ductile
cast iron prepared according to the invention is not subject to the adverse fading effect associated with prior art methods and materials. It is also noteworthy that when the agent and method of the invention are employed in the production of ductile cast iron there is no significant decrease in the residual zirconium and magnesium content of the iron due to holding time after treatment and prior to casting.

The residual content desired in the ductile cast iron prepared by the method of the invention should be between 0.03% and 0.5%, preferably between 0.1% and 0.3% and the residual magnesium should be between 0.01% and 0.3%, preferably between 0.03% and 0.1%.

Test No. 55 shows the effect of heating a test specimen from test No. 5 at 900° C. for one hour. It will be seen that the heat treatment while slightly lowering the yield and tensile strength had the effect of more than doubling the ductility of the specimen as measured by elongation and reduction in area.

In practicing the method of the invention it is desirable that the molten bath of cast iron be within the temperature range of 1400 to 1550° C. at the time of the addition of the agent of the invention.

Inoculation of the treated iron may be made entirely in the bull or master ladle after the addition of the agents of the invention or each casting ladle of treated molten metal may be separately inoculated. Sufficient time should be allowed after inoculation for the inoculant to go into solution in the treated iron before pouring. Any effective inoculant may be employed such as calcium-silicon, ferrosilicon, other silicon-bearing alloys, graphite, vanadium and aluminum. Sufficient inoculant should be introduced into the treated molten metal to graphitize the primary iron carbide.

The presence of phosphorus in amounts normally encountered in cast iron does not hinder the ability of the agent and method of the invention to produce spheroidal graphite but does have an adverse effect upon the ductility of the cast material.

The presence of sulphur does not affect the operation of the process of the invention but low sulphur is desired as the magnesium in the agent of the invention reacts with any excess sulphur necessitating larger additions of the agent than otherwise would be required. It is recommended that if the sulphur is higher than desired, the molten cast iron be subjected to any well known desulphurization treatment with sodium carbonate, calcium carbide or the like prior to treatment with the agent of the invention.

The term cast iron employed in this specification and in the claims refers to both hypereutectic and hypoeutectic iron containing carbon in an amount between about 2% and 4.5%; silicon in an amount between about 1% and 5%; manganese in an amount between about 0.3% and 4%; phosphorus between 0.01% and 0.75%, preferably not above 0.25%; and sulphur desirably as low as practicable but preferably not exceeding 0.25%.

Alloying elements such as chromium, molybdenum, and other special materials may be introduced in amounts necessary to give the iron the particular properties desired without changing its essential character.

What is claimed is:
1. In a method of producing ductile cast iron, the improvement which comprises preparing a bath of molten cast iron within the temperature range of about 1400 to 1550° C.; preparing a mechanical mixture of comminuted zirconium-bearing material and comminuted elemental magnesium; introducing into said molten bath of cast iron said mechanical mixture of comminuted zirconium-bearing material and comminuted elemental magnesium in an amount sufficient to incorporate in said cast iron a residual zirconium content of between 0.03% to 0.5% and a residual magnesium content between 0.01% and 0.2%; thereafter introducing an inoculant to said cast iron in an amount sufficient to graphitize the primary iron carbide in said cast iron; holding said molten cast iron until the bath becomes substantially quiescent and thereafter casting said molten iron.
2. In a method of producing ductile cast iron, the improvement which comprises preparing a bath of molten cast iron within the temperature range of about 1400 to 1550° C.; preparing a bonded mechanical mixture of comminuted zirconium-bearing material and comminuted elemental magnesium; introducing into said molten bath of cast iron said bonded mechanical mixture of comminuted zirconium-bearing material and comminuted elemental magnesium in an amount sufficient to incorporate in said cast iron a residual zirconium content of between 0.1% and 0.3% and a residual magnesium content between 0.03% and 0.1%; thereafter introducing an inoculant to said cast iron in an amount sufficient to graphitize the primary iron carbide in said cast iron; holding said molten cast iron until the bath becomes substantially quiescent and thereafter casting said molten iron.
3. An addition agent for the production of ductile cast iron from molten cast iron which agent comprises a mechanical mixture of a comminuted zirconium-bearing material and comminuted elemental magnesium, said agent containing, in addition to incidental impurities, between 10% and 30% elemental magnesium metal, between 10% and 50% zirconium, between 1% and 45% silicon and between 5% and 45% iron.
4. An addition agent for the production of ductile cast iron from molten cast iron which agent comprises a bonded mechanical mixture of a comminuted zirconium-bearing material and comminuted elemental magnesium, said agent containing, in addition to bonding material and incidental impurities, between 15% and 30% elemental magnesium metal, between 15% and 30% zirconium, between 20% and 45% silicon, and between 5% and 35% iron.

CHARLES M. OFFENHAUSER.

REFERENCES CITED

The following references are of record in the file of this patent:


American Foundrymen, February, 1949, pages 30 to 37. Published by the American Foundrymen's Society, Chicago, Illinois.

Canadian Mining and Metallurgical Bulletin, July 1949, pages 338 to 348. Published by the Canadian Institute of Mining and Metallurgy, Montreal, Canada.