METHOD FOR HOMOGENEOUS GERMINATION INOCULATION OF CAST IRON AND STEEL AND PRODUCT

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No Drawing. Filed Jan. 5, 1966, Ser. No. 518,784

Claims priority, application France, Jan. 18, 1965, 2,307; July 8, 1965, 23,977
10 Claims. (Cl. 73—55)

The present invention relates to a process for the production of improved cast iron and steel and more particularly to a homogeneous germination inoculation process for liquid cast iron and steel and the product obtained thereby.

Many attempts have been made in the prior art to alter or direct crystallization of solidifying cast iron by adding ferrosilicon, silicocalcium, silicomanganese-zirconium, etc., to the casting ladle. These processes result in the multiplication and refining of graphite particles, austenitic grains and eutectic crystals in the products obtained; however due to the particular nature of the inoculating agents, these processes also result in heterogeneous inclusions in the products.

The iron and steel industry has carried out many tests to alter the cooling and crystallization of steel cast in ingot molds, particularly effervescent steels, by adding various materials, such as scales or iron ore, to the bath. The results are not conclusive either because the added material does not blend with the bath or the steel obtained is contaminated with undesirable inclusions after solidifying.

It would appear that such failures were mainly due to the composition of the inoculating agents and the macroscopic particle sizes thereof which are much greater than that of the elements added of iron.

Particular problems have also been experienced by the industry in the inoculation of effervescent steels, especially where several ton castings of more than 2-meters in height are involved. Although conventional techniques result in a product having a very thin skin, with a very homogeneous surface offering attractive stamping and wire drawing properties, there occur in such ingots undesirable segregations of elements such as carbon, manganese and sulphur. The segregation of the sulphur becomes more marked as the mass of the ingot increases.

When such ingots are blocked by adding aluminium or by mechanical capping, the phenomenon is appreciably limited but only second-class products are obtained, especially from the standpoint of weldability and deep stamping.

Accordingly, it is an object of the present invention to provide an improved process for inoculating cast iron and steel to obtain an improved degassing and purification of the material so treated.

It is a further object of the present invention to provide an improved process for inoculating effervescent steel ingots to decrease segregation at the tops thereof.

Other objects and the nature and advantages of the instant invention will be apparent from the following description.

According to the present invention an improved homogeneous germination inoculation is obtained by adding to the ingot molds or the casting ladle specific and controlled amounts of highly pure powdered sponge iron of a given composition, crystal structure and particle size. By utilizing this inoculating agent, surprising results and products of outstanding quality were obtained by changes in the cooling and crystallization processes of treated cast iron and steel.

According to the present invention, the powdered sponge iron inoculating agent particularly suitable for the homogeneous germination of cast iron and steel have particular characteristics which are defined within rather narrow limits. The characteristics of the sponge iron depend upon the nature of the starting material and the operating conditions during the manufacture thereof. A material that may be prepared by the direct iron or reduction process is described in U.S. patent application Ser. No. 444,607, filed Apr. 1, 1965. This process includes the following successive steps:

1. Preheating the mineral to 900–1000° C. and the hydrogen rich reducing gas to 800–850° C.;
2. Primary reducing step using a fluidized bed at 700–750° C., to reach a reduction of about 60–75%;
3. Cooling of the partially reduced product to a temperature below about 250° C.;
4. Reheating the partially reduced product to 380–450° C. and of a reducing gas to 700–750° C.; and
5. Final reduction in a fluidized bed at 550–580° C. to reduce the partially reduced iron oxide to 90–99% of total reduction.

This material, which may be the product of step 2 or step 5 above, has the following characteristics.

Chemical analysis:

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>77.0 to 99.9%</td>
</tr>
<tr>
<td>FeO</td>
<td>0.0 to 100.0%</td>
</tr>
<tr>
<td>FeO2</td>
<td>0.0%</td>
</tr>
<tr>
<td>Sn, Zn, Cu, As</td>
<td>Indeterminable traces</td>
</tr>
<tr>
<td>Mn</td>
<td>≤0.2%</td>
</tr>
<tr>
<td>Ni, Cr, Co</td>
<td>0.0 to 0.01%</td>
</tr>
<tr>
<td>Si, S, P</td>
<td>≤0.01%</td>
</tr>
<tr>
<td>Oxygen (in the form of FeO)</td>
<td>0.0 to 22.0%</td>
</tr>
<tr>
<td>Nitrogen and hydrogen</td>
<td>Traces</td>
</tr>
<tr>
<td>SiO2+Al2O3+TiO2</td>
<td>≤1.0%</td>
</tr>
</tbody>
</table>

Physical analysis:

<table>
<thead>
<tr>
<th>Particle size</th>
<th>40 to 2,000 microns (preferably 40 to 400 microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent density</td>
<td>2.3 to 3.0</td>
</tr>
</tbody>
</table>

The amount of inoculating agent which should be added to liquid cast iron or steel baths may be as high as 5.0% by weight, depending upon the FeO content thereof and the required characteristics of the final product.

Due to the high state of division of the sponge iron, the oxygen combined in the form of FeO, together with the air confined in the microscopic grain cavities, an outstanding reactivity is imparted to the material with respect to oxidizable elements and uncombined dissolved gases in the liquid cast iron or steel baths. Furthermore, the very high porosity and small particle size of the inoculating agent result in a great dispersion thereof in the bath to affect the cooling and crystallization rates of the bath in a very homogeneous way throughout the mass thereof. Lastly, the elemental particles consisting of reticular piling of number of atoms according to the body-centered cubic system have a homogeneous germinative action owing to the structure analogy thereof with the major constituent of the bath both by epitaxy during the solidification and by modification of bath concentration in the vicinity of each inoculating grain.

Among the specific effects resulting from such an inoculation is the degassing of the cast iron and steel. It is known that all cast irons and most steels contain some proportion of dissolved gases, especially hydrogen and nitrogen. When specific amounts of the powdered sponge iron are introduced into the liquid bath, the elemental grains are spontaneously disintegrated owing to the brutal expansion of the air confined therein. The broad particle
FeO + C = Fe + CO — 37.9 Cal.

The endothermicity of the reaction together with the mass cooling due to the inoculating agent causes an immediate and sensible lowering of dissolved gas solubility while carbon monoxide bubbles ascending to the surface swirl along a large proportion of the gases.

In the case of treatment of low carbon steel, degassing should be carried out by adding an amount of finely divided carbon to the inoculating agent to start the reactions. However, if the treatment of the present invention is applied to quarter hard steels, such as the effervescent steels for deep stamping, high magnetic permeability steels or some alloy steels of austenitic nickel-chromium 18/8 grade, wherein it is difficult to lower the carbon content to values under 0.05% on account of peroxidation hazards, this outstanding reactivity of the iron powder with respect to carbon permits the simultaneous degassing and decarburization under excellent conditions without other bath elements being affected at casting temperature, especially silicon and manganese.

A further advantage of the invention is that each particle of inoculating agent liberated by dissociation of the powdery aggregates causes the initiation of homogeneous crystallization due to mass cooling, a change in the iron concentration in the vicinity of the particles and epitactic rearrangement from the particles. Thus, the finely divided state of the iron powder has a positive effect upon germination and the growth rates of the germs while imparting to the finished product a finer structure with smaller intercrystal interstices corresponding to the absence of micronoporosity. The dendritic segregation process is considerably altered due to the shortening of the solidification front and the final product is sounder and less liable to internal stresses.

Another effect of the use of inoculating iron powders of the above described characteristics is to purify the cast iron or steel baths treated quite appreciably. Indeed, the non-metallic constituents contained therein in very low concentrations, such as SiO2 and Al2O3 for instance, are to be found again in the medium in the nascent and highly dispersed state. As they are insusceptible under the conditions of the treatment, they quickly ascend to the surface by gravity carrying along a large proportion of the elements contained in the bath.

The influence of inoculation on degassing and carbon and silicon improvement of the bath also results in the modification of hardening and depth thereof in the case of white and mottled chilled-cast irons. With the addition of 1.5% by weight of iron powder of particle size ranging between 40 and 400 microns having an FeO content of 24.0%, a minimum hardening depth is noted.

The inoculation according to the present invention has a very important influence on the crystal texture itself of the cast iron and steel.

Thus, by using the techniques of this invention, it is possible to cause the ferritization of cast iron or the partial transformation of γ iron into α iron in steel, especially in the low carbon and high silicon grades intended for making magnetic sheets wherein embrittlement under heat and internal stresses are substantially reduced and the magnetic permeability is markedly improved.

The ferritizing effect of these iron powders on cast iron results from the evolution of some amount of nitrogen and hydrogen, which gases are stabilizers for iron carbides in the form of cementite and perlite. Thus, a 1.5% by weight inoculation of pure sponge iron containing 24.0% of FeO causes the direct formation of from 12.0% to more than 20.0% of ferrite according to the operating temperature. The treatment is far more effective where it is carried out on spheroidal-graphite cast irons, ferritization being then facilitated to such an extent that it is possible in many cases to avoid the subsequent thermal ferritizing treatment of castings with all the hazards of deformation involved, especially for thin castings.

On the other hand, malleable black-heart cast irons and especially nodular graphite ones do not permit the elimination of the thermal ferritizing treatment. The duration thereof, however, is largely shortened owing to the sensible improvement in the ability to ferritizing imparted thereto by the treatment.

Generally speaking, it has been ascertained that castings made from this sponge iron-treated cast iron are much more homogeneous than those from untreated cast iron, the latter consequently being subject to an appreciable increase in working-surface hardness and bending strength results.

When the process of the invention is applied to effervescent steels, it was found that the turbulizing result was more violent but was of shorter duration, and allowed better peripheral cooling and quicker expulsion of dissolved gases. When casting more than 5-ton ingots, it was found that there was a reduction in effervescence time of about a half to two-thirds when 2% additions of the powdered sponge iron were effected.

By modifying the effervescence it is possible to limit the amounts of control aluminium which results in the reduction of embrittlement aluminium-nitride content of the metal and the obtaining of a less contaminated skin.

This homogeneous germination inoculation procedure permits the casting of effervescent steel ingots having heights exceeding 1.8—2.0 meters, and the use of continuous casting in blooms or slabs.

It has been found that excellent results are achieved in the treatment of effervescent steel by the use of delayed blocking by the delayed addition of the powdered sponge iron powder to the mass after the initial effervescence has slowed down by the evolution of most of the gases. A revived turbulence is obtained by this delayed addition by reacting available oxygen in the form of FeO with segregated elements thus enriching the unsolidified part of the ingot. Simultaneously, the convection movement is accelerated repelling towards the center the equiaxed solidification front and secondary blisters that assume the appearance of primary ones. The second effervescence affects the molten metal core to a rather great depth by a thermostep effect due to the endothermicity of the reactions and heat absorption by the cold iron powder introduced into the bath, involving gas bubbles and, should the occasion arise, inclusions towards the top. Owing to the texture of the sponge iron, the reaction takes place at high speed and pure iron grains then act as homogeneous germs of equiaxed crystallization. The solidification front of dendrites being shortened, the accelerated solidification is carried out without austenitic grains becoming larger.

Effervescence is then quickly marked and segregation occurs no longer as consolidation proceeds.

The amount of sponge iron used with effervescent steels may run as high as 5% of the ingot weight according to the FeO content thereof, but excellent results are achieved with much smaller amounts of about 0.2% to 0.7%. Thus, by adding 0.3% by weight iron containing 36.3% of ferrous oxide to a 5-ton steel ingot, 8 minutes after casting, a decrease of 0.02% of initial carbon, of 0.1% of manganese and of 0.01% of sulphur in the
5 ingot top is noted which results in a higher homogeneity of the mass. Further, total solidification time is reduced by a fourth to a third.

It will be obvious to those skilled in the art that various changes may be made without departing from the spirit of the invention and therefore the invention is not limited to what is described in the specification, but only as indicated in the appended claims.

What is claimed is:

1. A process for the homogeneous germination inoculation of liquid cast iron and steel which comprises adding thereto up to approximately 5% by weight of non-erythrocytic powdered sponge iron prepared by the reduction of iron ore and containing from 77.0% to 99.0% of free and oxidized iron, the oxygen in the form of FeO being present from 0-22% by weight.

2. The process of claim 1 wherein the sponge iron has a particle size of from 40-2000 microns.

3. The process of claim 1 wherein the sponge iron has a particle size of from 40-400 microns.

4. The process of claim 1 wherein the sponge iron has an apparent density of between 2.3-3.0.

5. The process of claim 1 wherein the steel is an effervescence steel.

6. The process of claim 5 wherein the sponge iron is added to the solidifying ingots.

7. The process of claim 5 wherein the sponge iron is added to the mass after the initial effervescence has slowed down resulting in reviving turbulence.

8. The process of claim 1 wherein the material being treated is a low carbon steel and finely divided carbon is simultaneously added with the powdered sponge iron.

9. The process of claim 6 wherein the height of the ingot cast exceeds 1.8 meters.

10. The product formed by the process of claim 1.

No references cited.

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