METHOD OF APPLYING EXOTHERMIC MATERIAL TO THE HOT-TOP OF STEEL

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This invention relates to the casting of large steel ingots weighing at least 3000 pounds from killed steel in molds having refractory hot-tops, and has for its object the provision of an improved process for casting such ingots. Our invention is concerned with the casting of the steel and the treatment of the metal in the hot-top to minimize or eliminate pipe and to materially reduce the loss of metal to be cut from the ingot resulting in a more efficient production of steel ingots of improved quality.

In accordance with our invention, we modify the conventional ingot casting technique by pouring much less steel into the hot-top and immediately after pouring arrest the normal cooling, and then after a relatively long waiting time release on the metal in the hot-top a very appreciable quantity of heat from the reaction of highly exothermic materials added to the metal in the hot-top to effect a further appreciable delay in the normal cooling rate and thereby feed the ingot and minimize or eliminate the pipe.

Ingots of the type with which the invention is concerned are relatively large and substantially square or circular in cross-section, and it is the usual practice in casting them to use a refractory hot-top of various shapes and proportions and to pour a very appreciable amount of steel into the hot-top to feed the shrinking ingot and cause the pipe to form in the hot-top which is cut off. The hot-top may be of smaller cross-sectional dimensions than the mold and it may taper inwardly towards the top. Such hot-tops receive a relatively high level of steel. Other hot-tops are virtual extensions of the ingot mold and receive a relatively low level of metal. Regardless of the kind of hot-top, it is the usual practice to pour from 11% to 22% of the total volume of steel into the hot-top, depending on the size of the ingot and the kind of steel. Approximately 3½% of the volume of the ingot is required to feed the ingot due to its shrinkage.

In accordance with our invention, we pour the ingots “short” and by that we mean from about ¾ to ½ the height of metal usually poured into the hot-top. On a volume basis, we pour from 3½% to 11%, preferably from 5% to 7% of the volume of the ingot, into the hot-top.

After the ingot has been poured we wait an appreciable time before adding the highly exothermic material to effect the final heating of the steel in the hot-top. By “highly exothermic material,” we mean compositions comprising one or more metals which react with an oxygen-bearing material of the composition to liberate a large quantity of heat in a reaction ignited by contact of the composition with the steel in the hot-top. In accordance with our present preferred and improved process, we prolong the waiting time either by arresting the dissipation of heat by use of a thermal insulation or by the addition to the steel in the hot-top of mildly exothermic material. After the steel in the hot-top has cooled to a point approaching solidification, we add a highly exothermic material, such as a mixture of iron oxide, preferably FeO, powdered aluminum and slag-forming material, to the steel in the hot-top to release and add to the steel from about 250 to 425 kilogram calories per 100 pounds of steel cast. This reheats the steel in the hot-top and enables it to feed the steel in the ingot mold and also to cause any pipe to form in the hot-top rather than in the ingot.

When alloy steels are being cast, we may substitute for all or a part of the iron oxide an oxide of the principal alloying metal, for example manganese oxide, nickel oxide, chronic oxide, etc., so that the reduced metal will be added to the steel in the hot-top and thereby maintain the requisite analysis. Special highly exothermic materials are sometimes necessary for special work. For example, these can be made to produce metal of 12—14% chromium, or of a normal 18—8 stainless steel composition, or of a 12—14% manganese steel. It can also be made to produce many other special analyses. The alloy components are supplied by the oxide of the alloy desired or in some cases by the use of ferroalloys, such as ferro-manganese, or even pure metal, the balance arrived at being based on economics and obtaining the proper heat balance roughly equivalent to that obtained in the iron oxide-aluminum-slag relationship mentioned above. These special highly exothermic products are sometimes necessary to offset a tendency towards deleterious effects and/or segregation obtained in the upper portion of large ingots. The smaller the ingot the less necessity for using a special highly exothermic material and also the higher volume of metal used in the hot-top, the less necessity of this special highly exothermic material. That is to say, on ingots where 10—11% is used in the hot-top there appears to be no necessity in using the special highly exothermic material, but when a low volume is used in the hot-top and on ingots of 20 inches in diameter and larger, this becomes a necessity. In addition, on smaller ingots where no iron is desired, such as on special nickel base super alloys, highly exothermic material can be made using nickel oxide as a base instead of iron oxide and thus eliminate any possibility of contamination. The alloys mentioned should not be construed as to limit the invention towards particular alloys but are only given as examples in how special highly exothermic compositions can be employed in the same manner as the iron oxide-aluminum composition.

Our invention is concerned with the casting of ingots weighing at least 3000 pounds which are either substantially square or circular in cross-section, being at least 16 inches in diameter for square ingots and at least 19 inches in diameter for circular ingots, and is applicable to all larger ingots including the largest ingots cast, for example, those around 50 inches in diameter and larger, weighing many tons.

An example of the practical application of our invention in normal practice, ingots in the neighborhood of 500 to 625 square inches in which the cross-section is close to being square presently require pouring a hot-top volume of approximately from 11 to 22%. Small ingots are in the small end of this range, and very large ingots, meaning ingots from 36 inches in diameter and up, are
3 in the high end of this range. For a specific example, a 22 x 25, 18-8 type 304 stainless steel ingot is normally made with a hot-top volume of 13-15%. When using the improved process of our invention in casting similar ingots, we pour but from 5 to 7% of steel into the hot-top. For certain ingots we may approximate the pouring of 3.5% of the steel in the hot-top as this is approximately the theoretical shrinkage factor for steel going from the liquid to the solid state and to 2% of our invention is properly practiced even on the largest ingots no more than 11% is required, and on ingots of this type formerly 22% hot-top volume was required. This reduction in hot-top volume amounts to pouring the ingot from 1/2 to 1/2 the height inside the hot-top as used in normal practice, and usually, these pouring heights are based on the normal hot-top cross-section to ingot cross-section. If the hot-top is the same cross-section as the ingot instead of smaller, the pouring height would be on the low side or even less than 1/2 of the volume heretofore mentioned. The height to pour into tapered hot-tops must be calculated on a basis of height versus volume. The pouring volume and/or height will also slightly change in relation to the type of steel being poured, i.e., the higher shrinkage steels being poured slightly higher and the lower shrinkage steels being poured slightly lower. The next step in our invention is the waiting time. As heretofore mentioned, a mildly exothermic or insulating material should be added to the metal surface immediately after pouring to the desired height is completed. It is important to determine the waiting time objectively to have the greatest difference possible in the quantity of heat between the metal in the hot-top portion and the metal in the ingot mold portion. A limiting factor on all waiting time is the bridging effect of crystals meeting in the center portion of the ingot caused by solidification starting from the outside edges. These crystals can grow together leaving small pools of liquid metal beneath them and this latter portion of liquid metal leaves small shrinkage voids when solidification is completed. These small islands of shrinkage would be caused by the feed metal being chocked off from them by the bridges solidifying in layers above them as stated before.

In relation to the waiting time, the addition of other materials, such as thermal insulation or heat producing materials, immediately after pouring allows this time to be greatly extended. The extension of this waiting time is extremely important to the satisfactory results gained by the process of our invention. Materials to be added to extend this waiting time can be of the mildly exothermic type, such as those having carbonaceous material as a base, or slow heat producing materials, such as aluminum drosses with chemical oxidizing agents, such as sodium-nitrate, potassium-nitrate, sodium-chlorate, manganese dioxides, and/or other oxygen producing agents together or individually, or can be of the insulating variety, such as diatomaceous earth, lime, crushed cork, expanded mica, perlite, asbestos, rice hulls, pumice, fly ash, and similar inert or relatively inert materials with a fairly good insulating property. In practicing our invention in casting square ingots above 16 inches in cross-section or round ingots above 19 inches in diameter, it is definitely superior to add one of the general types of material mentioned above to the steel surface in the hot-top immediately after pouring has been completed. The mildly exothermic and carbonaceous materials should be added in amounts ranging from a 1/4 inch to 1/2 inch layer. The insulating materials should be added in amounts ranging from 2 to 5 inches in thickness. The density of the insulating materials would affect the thickness of the layer, the smaller amounts of both materials being used on the smaller sized ingots and the larger amounts on the larger ingots. More of these materials can be used but an excess does not serve any useful purpose.

After the steel has cooled to the desired degree, the remains of the material placed in the hot-top to extend the waiting time may be removed if it is unduly bulky or will interfere with the subsequent treatment and then the highly exothermic material is added to the steel in the hot-top. While the actual waiting time may vary from 20 minutes to 120 minutes depending on the size of the ingot, we can determine the minimum time by dividing the square of the mean ingot diameter by 1300 when the steel is poured at around 200° F. above its melting point. The objective of this determination is to determine the time just before bridging takes place in the ingot. Usually some solidification of steel takes place in contact with the hot-top at the end of the waiting time, but the time should not be delayed until solidification takes place in the center of the hot-top. When the waiting time is excessive, bridging will have taken place and shrinkage may be encountered in the interior portion of the ingot. In addition, excessive long waiting requires much heat from the highly exothermic material that is wasted in re-melting material already frozen around the hot-top portion of the ingot. A range of the optimum waiting times can be worked out for each size and type of ingot, the larger ingots having much higher optimum waiting times which can extend into hours for ingots above 50 inches in diameter. The pouring temperatures as well as the types of steels will have an effect on the waiting time, i.e., the higher pouring temperatures in relation to the freezing temperatures increase waiting times. Steels which solidify rapidly, tending to form large crystals over a wide solidification range, also have an adverse effect. Ingot mold shape also affects the waiting time.

The amount of highly exothermic material required will vary from around 0.25 pound per square inch in smaller ingots up to about 0.45 pound per square inch for the large ingots, of cross-sectional area in the hot-top. Ingots in the smaller range of from 16 inches to 30 inches would require from 0.25 to 0.38 pound per square inch and larger ingots would require from 0.35 to 0.45 pound per square inch. The highly exothermic material should all be added at one time. It then will react by itself producing high temperatures and a small amount of liquid metal and slag. Highly exothermic material can also be added based on the weight of the ingot. In this practice approximately 0.75 to 1.25 pounds can be added per 100 pounds of ingot weight. The smallest amount of exothermic material that can be used and still give satisfactory results from a quality standpoint will be found to be most economical but amounts in excess of the minimum requirements may be used without detrimental effects.

We may use any suitable exothermic material in the final heating of the steel in the hot-top, such as various types of Risotherm, a product of Exomet Incorporated, Conneaut, Ohio, or mixtures of metals which liberate a large amount of heat such as aluminum, silica, etc., with oxidizing agents such as metal oxides or sodium nitrate, etc.

In producing steels which do not have a large percentage of alloying metal, we prefer to use an exothermic material comprising iron oxide, preferably Fe-O, aluminum powder, and slag-forming ingredients, all of which are properly sized and intimately mixed. Exothermic materials in which the iron oxide and aluminum powder are in stoichiometric proportions produce steel containing anywhere from 0.10 to 0.15% carbon and are undesirable for the purpose of our invention. In one aspect of the process of our invention, we use a highly exothermic material having an appreciable excess of iron oxide over the aluminum, say, at least 12% in excess of the stoichiometric amount, preferably from 15% to 23% excess, by means of which we produce metal from the reaction containing less than 0.09% carbon. One of the products of
the exothermic reaction is aluminum oxide but the exothermic material comprises an appreciable amount of other slag-forming materials. While the excess of iron oxide enters and becomes a part of the slag, it is advantageous to include in the material other slag-forming materials free of carbon. When using an excess of 12% iron oxide, it is necessary to add about 17% of other slag-forming materials. As the excess of iron oxide is increased, the other slag-forming material is decreased but the excess of iron oxide should not exceed about 23% because the slag will become foamy and unmanageable. As a result of the exothermic reaction, there is produced a relatively deep upper layer of slag, comprising the aluminum oxide, the excess iron oxide, and the added slag-forming materials, having a high heat content and low thermal conductivity which acts as a heat reservoir as well as an insulating top for the ingot. The exothermic material ignites at about 1900° F.

Creating intense heat, the temperature rising to over 4000° F. The heat greatly increases the temperature of the metal in the hot-top which feeds the ingot as it undergoes shrinkage. Moreover, this heating permits the accumulated gases to escape and dense metal to form at the top of the ingot.

The importance of using an excess of iron oxide in the exothermic mixture is manifested largely by the absence of carbon pick-up by the metal produced and by the lack of violence in the exothermic reactions. The high proportion of iron oxide results in exothermic metal low in carbon and the escape of carbon oxides from the region of the ordinary pipe is not violent.

Thus, there is less heat loss and the exothermic material becomes more efficient, allowing less material to be used to gain similar quality results. Attempts made heretofore to use exothermic materials in the hot-top have not produced results more beneficial than the use of relatively deep steel in the hot-top. It has been cheaper to use more steel in the hot-top than to use highly exothermic material. In contradistinction, we are able to accomplish surprising results with but a relatively small amount of the exothermic material. The increase in ingot yield has amounted to from 3% to 12% and will vary widely depending on the type and grade of steel used, the size of the ingot mold, the design of the ingot mold, the type of refractory hot-top used, and the general teeming and pouring practice.

The following are three types of highly exothermic material suitable for use in the process of our invention:

For use on 12% manganese steel

60–64% FeO₃.
19–20% Al.
10–12% Ferro manganese.
12–15% Slag forming materials.

For use on chromium steel

61–65% FeO₃.
3–4% Cr₂O₃.
8–9% Ferro chromium.
22–24% Al.
4–6% Slag forming materials.

For use on nickel steel

60–65% Nickel oxide.
16–17% Aluminum powder.
20–26% Slag forming materials.

The foregoing exothermic materials are in a pulverulent state and intimately mixed together. The slag forming material may consist of CaO, SiO₂, CaF₂, Fe₂O₃ and FeO, either alone or in admixture.

The following is an example of a mildly exothermic material of the type which may be added to the hot-top immediately after pouring:

Aluminum dross........ 70–75% (20–25% aluminum).
Iron oxide............. 8–12%.
Clay.................. 8–10%.
Sodium nitrate.......... 8–10%.

The following are examples of steel ingots produced in accordance with our invention:

<table>
<thead>
<tr>
<th>Metal Cast</th>
<th>12-14 Mn Steel</th>
<th>18 Cr-8 Ni</th>
<th>L0% C, 1% Cr, 3% Mo, 6% V.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot Top</td>
<td>Chs—18° x 21°</td>
<td>Chs—10° x 12°</td>
<td>Refractory 30° I. D. 20° x 20°</td>
</tr>
<tr>
<td>Weight of Ingot</td>
<td>6,000 lbs</td>
<td>6,000 lbs</td>
<td>44,000 lbs</td>
</tr>
<tr>
<td>Weighting Time</td>
<td>40 Min.</td>
<td>40 Min.</td>
<td>120 Min.</td>
</tr>
<tr>
<td>Material Added Initially to Increase Delay Time</td>
<td>20 Lbs.</td>
<td>20 Lbs.</td>
<td>75 Lbs.</td>
</tr>
<tr>
<td>Amount of Heat Added by Addition of Highly Exothermic Material</td>
<td>4,000 Kilo. Cal.</td>
<td>4,000 Kilo. Cal.</td>
<td>125,000 Kilo. Cal.</td>
</tr>
<tr>
<td>Weight of Highly Exothermic Material</td>
<td>100 lbs.</td>
<td>100 lbs.</td>
<td>400 lbs.</td>
</tr>
</tbody>
</table>

1 Mildly exothermic materials described above.
2 Highly exothermic materials described above for use on such steels.

This application is a continuation-in-part of our co-pending application Serial No. 204,684, filed January 5, 1951. We claim:

1. In the casting of large steel ingots weighing at least 3000 pounds from killed steel in molds having a refractory hot-top, the improvement which comprises pouring the steel in such amount that the hot-top contains from 3 1/2 to 11% of the total steel cast, applying to the steel in the hot-top a material which delays solidification, allowing the ingot to cool for a time varying from 20 minutes for 3000-pound ingots to 120 minutes for large ingots, and then applying to the steel in the hot-top an exothermic material in an amount such as to release on ignition from 250 to 425 kilogram calories of heat per 100 pounds of steel poured.

2. In the process of claim 1, determining the minimum waiting time by dividing the square of the mean diameter of ingot by 1300 when the steel is poured at a temperature about 200° F. above the solidification temperature of the steel.

3. In the process of claim 1, applying to the steel in the hot-top immediately after pouring a thermal insulating material to delay the normal cooling for at least ten minutes.

4. In the process of claim 1, applying to the steel in the hot-top an exothermic material which undergoes oxidation with the addition of heat to the steel in the hot-top to delay solidification.

5. In the casting of large steel ingots weighing at least 3000 pounds from killed steel in molds having a refractory hot-top, the improvement which comprises pouring the steel in such amount that the hot-top contains from 3 1/2 to 11% of the total steel cast, applying to the steel in the hot-top a material which delays solidification, allowing the ingot to cool to a time just before bridging takes place in the ingot which is in excess of 20 minutes and before the steel solidifies in the hot-top, and then applying to the steel in the hot-top an exothermic material in an amount such as to release on ignition from 250 to 425 kilogram calories of heat per 100 pounds of steel poured.

6. In the improvement of claim 1, using an exothermic material consisting essentially of a metal and an oxygen-bearing compound that forms an oxide with the metal,
which material produces temperatures in the hot-top of about 4000° F.

7. In the improvement of claim 5, using an exothermic material consisting essentially of a metal and an oxygen-bearing compound that forms an oxide with the metal, which material produces temperatures in the hot-top of about 4000° F.

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