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ELIMINATION OF HYDROGEN FROM HEATS OF KILLED STEEL

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It is well known that hydrogen in killed steel is a source of blisters and flakes in the final rolled product, and results in the rejection of large quantities of valuable material. This is especially the case with stainless and other chromium steels.

The primary object of this invention is the provision of a mode of eliminating hydrogen or reducing it to that amount which the solidified steel can hold in solution, so as to eliminate or minimize blistering from this source, easily, quickly, safely and economically. We accomplish this object and others which will be set forth hereinafter or will be apparent to one skilled in the art upon reading these specifications, by that procedure of which we shall now describe an exemplary embodiment.

The actual amount of hydrogen which stainless steel, for example, can hold in solution just below its melting point, has not hitherto been known or published, so far as we are aware. Our researches have indicated that this amount is in the neighborhood of .0007% by weight. If a molten bath of stainless steel contains more than this amount of hydrogen, the excess above the solubility limit will be evolved during solidification of the metal, and will result in abnormally low shrinkage, indicative of internal cavities which form blisters in the final rolled metal. Conditions in the bath productive of abnormally low shrinkage in the ingot can occur at any time during the heat; but these conditions usually occur after the bath contains some silicon.

Baths of killed chromium bearing steel in the electric arc furnace have a tendency to absorb hydrogen. We believe that the hydrogen is absorbed when in a nascent state due to the dissociation of hydrogen bearing compounds at high temperatures, principally through the dissociation of moisture. When the bath is covered with a reducing slag which is non-conductive, the action of the arcs is to blow the slag away from the surface of the metal about the arcs, exposing it for the absorption of hydrogen. This hydrogen may arise from moisture in the air, but on occasion there may be a leak in the glands of the water cooling jackets about the electrodes, permitting water to be delivered to the atmosphere inside the furnace and sometimes to drip upon the metal itself.

The presence of hydrogen in the bath may readily be detected by what we term a "shrink test." In performing such a test a small quantity of the molten metal is merely taken from the bath, poured into a small test mold, and covered with an insulating material. When the metal

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freezes its shrinkage characteristics are immediately apparent. If the metal does not contain an excess of hydrogen it will shrink in volume about 3%, which will show up as a visible cavity in the extreme top of the test piece. If the metal contains an excess of hydrogen, the cavity will be abnormally small or the surface may even rise in the mold, and the cross section of the cast piece will show blow holes. Such shrink tests, performed at intervals throughout a heat, can be employed as a guide both to the duration of the treatment hereinafter outlined, and to that point or points, in the course of a heat, at which the treatment may be applied.

In the practice of our invention, we have found that if air, which has been thoroughly dried, is blown through the bath, it will remove contained hydrogen in an amount depending upon the quantity of air blown. As an indication of what is meant by thoroughly dried, we have found that air dried so as to have a dew point at approximately 20° below zero F. or lower is entirely satisfactory for our purpose.

As an example of procedure under our invention, in producing stainless steel in the electric furnace, we blow the thoroughly dried air at approximately ten pounds pressure per square inch through a gas pipe $\frac{3}{4}$ in. in diameter thrust through a furnace opening and immersed into the bath. The gas pipe is of ordinary iron, wrought iron or steel, and of a standard length, such as 15 feet. The submergence of the pipe in the bath causes it to melt away progressively so that it is necessary to keep thrusting it further and further into the bath. When one such pipe is no longer usable, another is employed, and so on until the required amount of air is blown through the bath. More than one pipe may be thrust into the bath at a time if desired.

The consumption of pipe in this fashion furnishes a fair measure of the air blown at a certain pressure. In commercial practice we have found that it usually requires about five "pipes" of air to lower the hydrogen content of a 10-ton heat to a value such that ingot shrinkage will be satisfactory. More or fewer "pipes" may be blown as indicated by the shrink test. It will be evident that the quantity of air blown may be otherwise measured, especially where an insulated conduit or other non-melting means is used for introducing the air into the bath. The pressure suggested is not limitative, and may be considerably varied, but is a good and safe operating pressure for the purpose. The use of too great pressure is likely to produce ebullition and spat-

tering in the bath, which it is desirable to avoid. It is especially desirable to avoid such turbulence in the bath as would result in the splashing of molten metal onto the raised arc electrodes, which metal, dripping back into the bath after having picked up carbon from the electrodes, might harmfully affect the carbon content of the melt.

The blowing of thoroughly dried air through the bath as herein set forth is effective in removing hydrogen, but does not significantly alter the bath characteristics in any other way if performed while the bath is under reducing conditions. As will be readily understood, reducing conditions are attained when the bath contains silicon or some other active deoxidizer or when the slag above the bath is high in silicon or its equivalent. Those skilled in the art will understand that it is usual in the production of chromium bearing steels to carry on the latter stages of the heat under a slag to which ferro-silicon or the like is added to return as much chromium as possible to the bath. When the blowing is done under reducing conditions, it produces negligible oxidation or decarburization, and causes no lack of cleanliness in the steel.

It is important that our treatment may be practiced when the bath contains a large part or all of the desired chromium content, providing silicon is also present. Under usual operating conditions the bath will contain substantially .10 to .30 silicon. The silicon is removed to a slight extent depending upon the duration of the blow; but it protects the chromium so that the latter is not oxidized to an appreciable degree. Hence, our treatment may be practiced, if desired, as substantially the last treatment to which the heat is subjected prior to tapping or pouring, or it may be practiced at any preceding stage at which its effect is useful. The treatment may also be repeated during the course of any heat, as shown to be desirable by test.

When the steel is formed or treated in the electric arc furnace, we stop the arc and raise the electrodes during the blow. It is not necessary to remove the slag, although this may be done with advantage under certain circumstances. The slag does not affect the removal of hydrogen by the blowing process; but hydrogen is lost, as we believe, by diffusion either into the air blown through the bath or into the atmosphere above the bath, the latter being an action which can occur effectively only in the absence of slag. Hence, removal of the slag will to some extent increase the quantity of hydrogen removed in a blowing process of given duration.

It will be understood that the air employed in our process may be dried in various ways and the particular manner of moisture removal is not a limitation on the invention. In practice we prefer to employ a drier having a chamber through which the air is passed and which contains calcium chloride or activated alumina as a drying agent, the latter usually being capable of lowering the moisture content further than the former.

Modifications may be made in our invention without departing from the spirit of it. Having thus described our invention in an exemplary embodiment, what we claim as new and desire to secure by Letters Patent is:

1. A process of producing commercially clean chromium-bearing steels of the stainless type, including the steps of producing killed steel in an electric arc furnace, thoroughly deoxidizing

the steel and during the finishing stage and close enough to the tapping to prevent hydrogen re-absorption, passing dried atmospheric air through the steel in said furnace under a pressure insufficient to produce excessive splashing to the extent of reducing the hydrogen in the steel to a value below its solubility in the solidified metal, and at a time when the steel contains residual deoxidizing agent, the steel being finished under a reducing slag.

2. The process claimed in claim 1 wherein the quantity of air so passed through the baths is sufficient substantially to remove by diffusion contained hydrogen in excess of that soluble in the solidified steel, as determined by a shrink test.

3. The process claimed in claim 1 wherein the quantity of air so passed through the baths is sufficient substantially to remove by diffusion contained hydrogen in excess of that soluble in the solidified steel, as determined by a shrink test, the air being dried so as to have a dew point not substantially higher than 20° F. below zero.

4. The process claimed in claim 1 wherein the said deoxidizing agent is silicon and wherein the quantity of said silicon present in the steel is at least substantially .10% of the steel mass.

5. The process claimed in claim 1 wherein the treatment with atmospheric air is carried on while the steel is under the finishing slag.

6. In a process of producing commercially clean chromium-bearing steel of the stainless type in the electric arc furnace, the steps of melting steel forming ingredients and adding chromium under the influence of electric heat from the arc electrodes in the furnace, adding ferro-silicon to displace chromium from a slag formed above said steel, thoroughly deoxidizing the steel by means of silicon with the provision of residual silicon in the steel, raising said electrodes and without removing said slag blowing through the molten steel atmospheric air dried so as to have a dew point not substantially in excess of 20° below zero F. under low pressure whereby to reduce the hydrogen content of said steel without producing significant oxidation or decarburization to a value not substantially in excess of the solubility of hydrogen in solidified steel, and thereafter tapping the steel from said furnace promptly to prevent hydrogen re-absorption.

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