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MANUFACTURE OF STEEL

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This invention relates to the manufacture of steel and more particularly to the control of the non-metallic inclusions which occur in steel.

In the manufacture of steel a certain amount of iron oxide is dissolved in the bath and must be removed for reasons well understood. It is therefore universal practice to add to the molten steel toward the end of the heat and in the ladle deoxidizers in the form of metals having a greater affinity for oxygen than iron has. The deoxidizers commonly used, are: manganese, silicon, titanium, aluminum, vanadium and magnesium. Manganese is a powerful deoxidizer but is incapable alone of completely deoxidizing a heat so that silicon is always used in conjunction with it. In basic open-hearth practice it is customary to add an alloy containing manganese or silicon, and metallic aluminum to the molten metal.

Although these deoxidizers successfully perform their deoxidizing function by robbing the dissolved iron oxide of its oxygen, the steel has but exchanged one oxide for another. Neither is desirable, but as iron oxide dissolves in the steel and separates out upon cooling, it must be removed, and the reaction oxides, being insoluble in the molten steel, are therefore the lesser of the two evils. But the fact that they happen to be a lesser evil does not mitigate their offense and their presence is a matter of concern to steel makers.

These reaction oxides are refractory and are not molten between 1600° and 1700° C. the temperature range of open-hearth furnaces, which means that they do not tend to agglomerate. This in itself would not be so bad, if the binary, ternary, quaternary, etc., compounds of their unions were uniformly fusible below or at operating temperatures, for then there would be a tendency toward agglomeration and uniformity. Unfortunately, however, the complex minerals which result from these unions are, for the most part, not substantially more fusible than the component oxides, and furthermore the fusibility curves of these minerals are exceedingly irregular so that although individual combinations may here and there show a low fusibility, a very slight change in the proportion of one of the constituent oxides will produce a product at best only pasty at furnace temperatures. Moreover, the time factor has an important bearing upon the formation of these minerals and the time normally elapsing between the introduction of the deoxidizers and the freezing of the steel in the ingot molds is insufficient to permit of anything like uniformity of reaction.

The result is that these refractory non-metallic deoxidation reaction products are scattered throughout the steel in varying physical conditions and in varying combinations. Some are sub-microscopic in size, that is too small to be detected by the microscope commonly used by metallographers; some are larger than this; some have been combined with other oxides to form products of indeterminate fusibility. The very fine inclusions cannot act as nuclei for grain formation, so that the steel is, in part at least, coarse grained. The larger inclusions, on the other hand, may and do act as nuclei for grain formation, and as a result the crystalline structure of the final product is non-uniform. The larger inclusions may also be scattered over comparatively large areas in such a way as to impart a dirty appearance to the steel. In short, these reaction oxides make the control of grain size and the production of a clean steel practically impossible.

As a specific example of conditions obtaining in a steel, let us consider the results of adding manganese, silicon and aluminum, the common deoxidizers employed in basic open-hearth practice. Neither manganese oxide nor silica is molten below 1700° C. and neither are the binary minerals formed by their union near the extreme ends of the curve. It happens, however, that from 50 to 85% MnO and 50 to 15% SiO_2 the resultant compositions have a uniform melting point of approximately 1270° C. As this is substantially below the temperature of the molten bath we have a fluid product which tends toward agglomeration into uniformly distributed particles large enough to act as nuclei for grain formation, and if time were allowed,

into particles large enough to float free of the bath. A combination of manganese and silicon might therefore be regarded as an ideal deoxidizer. As a matter of fact, so it is for some purposes, and is very successfully used in acid open-hearth practice. In making basic open-hearth steel, however, aluminum must be added to complete the deoxidation, and as soon as this happens the relatively fusible binary $MnO—SiO_2$ compositions with their wide range of low fusibility are transformed into much less fusible ternary $MnO—SiO_2—Al_2O_3$ compositions, the fusibility of which varies abruptly with slight changes in the proportions of the constituent oxides.

There are other refractory non-metallic impurities in steel besides the deoxidation reaction products which act in the same manner and are open to the same objections. In basic open-hearth practice, for instance, pieces of the furnace lining spall off and introduce particles of MgO into the bath; in making chrome alloy steel the highly refractory chromium oxide is undoubtedly present, and then there are also small refractory slag inclusions which are always to be found.

It is broadly the object of the present invention to control grain formation and make a clean steel by controlling these miscellaneous refractory non-metallic inclusions or impurities. I do this by adding to the molten steel a non-metallic flux of a specific gravity equal to or greater than that of the bath which will produce, in combination with any and all of these refractory impurities, a composition or compositions fusible below the temperature of the bath. The result is first an agglomeration of the non-metallic impurities into particles large enough to act as nuclei for grain formation, evenly dispersed throughout the bath. The longer the time allowed for the flux to act, the more complete the agglomeration and the larger and more widely separated the individual particles. Thus, the grain of the steel grows progressively coarser with the time elapsing between the introduction of the flux and the freezing of the metal. This agglomerating or "mopping up" action is not only effective in controlling the grain size, but by concentrating the inclusions, eliminates the peppery appearance which smaller inclusions often give to a steel.

The flux can be added to the metal in the ingot molds, in the ladles, in the furnace, and, conceivably it might be added prior to the introduction of the charge into the furnace. The earlier it is added, the longer time it has to work, the more complete the "mopping up", and the coarser the grain size. Thus, the finest grain is obtained by adding the flux to the metal in the ingot molds. If added in the auxiliary ladle in the so-called "double pour" process the grain is coarser, if added in the main ladle coarser still, and so on.

Although any flux having the properties discussed above would be suitable for the purpose, I have obtained excellent results by the use of a mixture of lead oxide, PbO, and sodium fluoride, NaF, in the proportion of eight parts of PbO to one part of NaF, the mixture preferably being fritted before use. Such a frit has a specific gravity high enough to insure its sinking in the bath. This frit has been added to the metal in the big ladle after the aluminum, in the auxiliary ladle, and in the ingot molds, in amounts of one-half pound per ton of steel. When added to the metal in the ingot molds the time elapsing before freezing and during which the flux can operate is about one-half a minute. The result is a very fine-grained structure. When added to the metal in the big ladle the time is about one hour and the grain of the resultant steel is coarser, although one hour is insufficient for a complete removal of the inclusions. Steel made by adding the PbO—NaF frit in the big ladle in the proportion of one-half pound of frit to one ton of steel has a grain size of about one-sixth of the average grain size of untreated steel.

As a specific example of what can be done in accordance with the present invention, I shall give the results of an actual test made on a chrome alloy steel. A heat having the following composition was used:

Carbon	.284
Manganese	.72
Sulphur	.021
Phosphorus	.018
Silicon	.22
Chrome	.94

A charge of seventy-five tons was melted in a basic open-hearth furnace, tapped into the main ladle and thence, through the auxiliary ladle teemed into the ingot molds. Three pounds of the lead oxide-soduim fluoride frit was added to the auxiliary ladle containing six tons of steel. Ingots made of the untreated and treated steel from the same heat were compared. Test pieces approximately one inch square were taken from corresponding places on both ingots, normalized one hour at 1575° F., air cooled, heated one hour at 1575° F., water quenched and drawn for one hour to 1100° F., and then turned down to .505″ diameter. The average of three test pieces taken from the untreated ingot showed an elongation of 15% and a reduction of 50.8%, whereas an average of three similar test pieces taken from the treated ingot showed an elongation of 17% and reduction of 63.7%. Samples of both the treated and the untreated steel were given comparative carburizing tests and the treated was uniformly finer grained than the untreated. The grains of the treated steel were on the aver-

age about one-seventh the size of the grains of the untreated.

By the addition of a non-metallic flux capable of forming with the refractory non-metallic inclusions, which always occur in steel as deoxidation reaction products, and impurities introduced from other sources, a product or products fusible below the temperature of the molten steel, I am enabled to produce a clean steel having improved physical properties and a uniform grain structure, the actual size of the grains being determined by the length of time elapsing between the addition of the flux and the freezing of the metal. The present invention is particularly applicable to basic open-hearth practice where refractory non-metallic inclusions have given the most trouble, and basic open-hearth steels treated in accordance with this invention compare favorably with the best electric furnace and acid open-hearth steels.

I claim:

1. The method of making basic open-hearth steel which comprises adding manganese, silicon and aluminum and then adding a non-metallic flux which forms with the resultant oxides a composition or compositions fusible at or below the temperature of the molten steel.

2. That improvement in the manufacture of steel having non-metallic refractory inclusions therein, which comprises adding a lead oxide-sodium fluoride frit thereto in the proportion of about one-half pound of the frit to one ton of the steel.

3. The method of controlling the grain size of steel having non-metallic refractory inclusions therein too small to act as nuclei for grain formation, which comprises incorporating with the steel a substance compounded of lead oxide and sodium fluoride which increases the fusibility of the inclusions, thus causing them to agglomerate and act as nuclei for grain formation.

In testimony whereof I affix my signature.

EARLE C. SMITH.