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METHOD FOR THE PRODUCTION OF
IRON AND STEEL

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The invention relates to a method for the production of iron and steel. More particularly, it pertains to the production of stainless steels and includes correlated improvements and discoveries whereby the properties of iron and steel are decidedly improved.

Further, the procedure may be employed with killed steel of alloy or of carbon grades, and the steel may be manufactured by conventional methods.

Steels, in the course of their manufacture absorb certain undesirable gases and substances which may impart poor engineering properties and may make the material difficult to shape or work.

A principal object of the invention is to provide a method whereby the foregoing disadvantages may be substantially wholly obviated.

A further object of the invention is to provide a method in accordance with which an iron and steel may be produced as a fine grain product, and having distinctive corrosion and oxidation resistance and high impact values at low temperatures.

A particular object of the invention is the provision of a method whereby the foregoing are achieved, and a product, namely an iron or a steel of enhanced properties, is obtained through the utilization of a rare earth oxide or silicide, preferably a plurality of the oxides, such as an ore or a concentrate thereof, with cerium oxide usually being present in a preponderant amount. This oxide will be more particularly referred to hereinafter for purposes of illustration.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

For the production of a steel which is highly resistant to corrosion and oxidation, and of a steel whose structure is such that it accords high impact values which are of especial import when the steel is to be used in cold climates, there are two generally accepted methods.

One method utilizes one or more of a number of commonly accepted alloys, and usually a minimum of 12% is employed. These alloys contain a member of the group consisting of molybdenum, chromium, nickel, tungsten, columbium, cobalt, tantalum, titanium, and zirconium, with varying amounts of silicone, copper, aluminum and manganese.

The second method uses the minimum amount of those metals and produces a grain in which the interstitial spaces are reduced in size and, thus, reduces the opportunity for corrosive and oxidation agents to attack the steel.

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In view of the fact that the alloys which are usually employed in producing heat resisting and stainless steels are in great demand and as such are hard to obtain at all times, we decided to attempt to improve these two types by producing a fine grain in the steel and to do this the molten steel has been treated with a composition composed essentially of oxides of the rare earth group.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the iron or steel possessing the features and properties, which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

In the practice of the invention, the properties of iron and steel, especially of stainless steels of high alloy type, such as the austenitic type and the chrome type, e. g. 19% chromium, and hard surfacing types as 3.5% nickel, 3% chromium, 7% molybdenum and 1% boron, are decidedly improved by the addition of an appropriate amount of a rare earth oxide, either singly or in compatible combination, and suitably of relatively fine size and may be in the form of a briquette which contains a mixture of rare earth oxides, and desirably containing a preponderant amount of cerium oxide, to a melt, that is to the liquid iron or steel.

More especially, the procedure comprises preparing an iron containing melt, adding metallics, which may contain chromium, manganese, molybdenum, nickel, tungsten, columbium, cobalt, tantalum, titanium, zirconium and silicon, thereto during furnacing and then deoxidizing, utilizing, e. g., ferrosilicon, calcium silicon, ferromanganese, and the like, with the addition of, and in conjunction with, the composition which, more particularly, contains a plurality of rare earth oxides having cerium oxide present in a preponderant amount.

The addition of the rare earth oxide may be effected at different phases of the melting and furnacing, and in a convenient and accepted manner. A suitable procedure is to add it to the ladle either before, during or after deoxidizers have been added, and desirably before the ladle is one-half full, that is while the ladle is less than one-half full. However, a preferred procedure is to place the oxide in the bottom of a ladle and cover over with a deoxidizer such as calcium silicide, or it may be placed in a thick walled pipe and the ends closed, and then placed in the bottom of the ladle where the liquid fer-

rous metal may be poured on top of it. Either method delays the action so that there will be sufficient liquid metal to allow a proper reaction therewith.

Further, we have found that when about 1-4 pounds of oxide have been added per ton of iron or steel, a very fine grain structure results. However, depending on the pouring temperature, the size of the mold, and the analysis desired, an amount of about 1.3 pounds of oxide to the ton has given beneficial results.

Stainless steels, which are usually a nickel-chrome combination, generally as-cast have large dendrites and these large dendrites cause the steel to break when any extra pressure is applied. However, when this class of steel is treated with rare earth oxide, there is produced a fine grain structure so that it is possible entirely to by-pass a forging operation. Moreover, it may be rolled as any normal steel to billet size.

In the manufacture of these steels, the usual accepted good practice is employed and in addition to it, care is taken to see that the steel is properly deoxidized, that it may be poured at a temperature which has been found to be lower than usual practice because of the fact that the treatment with the rare earth oxide increases the fluidity of the treated metal.

Various quantities of rare earth oxide have been tried and found to be effective. However, when excessive amounts have been added, the steel has been found to be extremely dirty and as such offered low resistance to oxidation or corrosion. Our method makes efficient use of the oxide and at the same time utilizes only a very small amount. We have definitely found that not more than four pounds of oxide per ton need be used provided that it is added to the melt as herein described and especially in the preferred manner.

As an illustrative embodiment of a manner in which the method may be carried out, the following examples are presented:

Example 1

A 1,000 pound heat was conducted with the steel obtained having the following analysis expressed as percentages:

Carbon	0.12
Manganese	1.75
Sulphur	0.035
Phosphorus	0.03
Silicon	0.03
Chromium	25.0
Nickel	20.25
Rare earth metal	0.03

and the remainder iron.

The furnace was charged with 482 pounds of plate and when melted, there were added during the furnacing 40 pounds of iron ore and 15 pounds of pig iron. The heat was then degassed and following blocking there were added during a period of about forty-five minutes 369 pounds of ferrochrome, 200 pounds of nickel, and 16 pounds 100% manganese.

When the heat had been adequately worked, there were added 12 pounds of nickel, and 2 pounds of ferrochrome, whereupon the heat was tapped and poured with 5 pounds of calcium silicide and 2 pounds of rare earth oxides having a preponderant amount of cerium oxide, being added to the ladle. The addition of the rare earth oxide was made subsequent to introduction of the calcium silicide into the ladle.

Example 2

A stainless steel was produced having the following composition:

	Percent
Carbon	0.12
Manganese	1.25
Silicon	0.2
Sulphur	0.03
Phosphorus	0.03
Chromium	24.0
Nickel	19.25
Rare earth metal	0.024

and the remainder being iron.

The heat was conducted as a 1,000 pound heat and the furnace was charged with 482 pounds of plate. When the charge had been melted, about 40 pounds of iron ore were added during furnacing, and following deslagging, there were added 369 pounds of ferrochrome, 200 pounds of nickel, as sheet nickel, and 16 pounds of 100% manganese.

After a second deslagging, 35.3 pounds of ferrochrome, 13.8 pounds of nickel, and 5 pounds 100% manganese were added to the melt. A short time before tapping and pouring, 1.5 pounds of calcium silicide, 3.7 pounds of chromium silicide, and 2 pounds of rare earth oxide, having a preponderant content of cerium oxide, were incorporated with the melt which was then tapped and poured in the usual manner.

The method herein described for the production of iron and steel leads to the formation of a fine grain structure which enhances the resistance to corrosion. Since there is, at most, only a small amount of the oxide remaining in the treated metal, it is believed that this condition is due to the small space between the grains which results from the reduction of the original dendritic structure and, hence, offers less interstitial space for attack.

The results show that there are several advantages which accrue to the user of a rare earth oxide when utilized in the manner described herein. Thus, one may use a standard material and obtain decided benefits due to its resistance to corrosion and oxidation. Further, the analysis may be varied so that less of a scarce and costly alloy will be employed to obtain the same results as the same untreated material with a larger amount of the alloy.

In the melting and casting of stainless steel, certain precautions have been found to be beneficial and are recognized as being proper practice. For instance, a good pouring temperature for grade 310 would be 2740° F. We have also found that the melt, after treatment in the ladle, should be poured immediately to insure quick freezing of the metal, and in some instances a thick walled ingot mold serves to effect the quick freezing. Due to the fact that slags cause reaction at the point of contact with the metal, it has been found that chilling the slag reduces such action, and this may be accomplished by the addition of slag making materials such as dolomite, burnt lime, and the like. Among the advantages attending the use of the oxide are the obtention of a fine grain as cast, and of higher impact values at lower temperatures. Such values are especially valuable in those types of steel which must function properly and safely at low temperatures, e. g. those in the arctic and antarctic regions.

Furthermore, when molten ferrous material has been treated with an oxide, or a combination of rare earth oxides, a fine grain results and later

certain definite improved physical and chemical characteristics are obtained. When steels are made in this way, it is highly desirable to make the steel so that this fine grain, as cast, persists. This is accomplished by casting at a relatively low temperature, and tapping or teeming as quickly as possible to solidify the material.

We have observed that if, after treatment with a substance which will endow it with these fine grain properties, the metal is allowed to remain in a liquid state for a long period of time, the fine grain gradually disappears and the resultant steel compares in almost every way, with an untreated steel. Moreover, when a melt is treated with the oxide and subsequently cast as a sand casting, whose solidification rate is very slow, a very small reduction in the grain size is obtained which indicates that retention for a long time after treatment in a liquid state allows the force which produces the fine grain to be dissipated and, hence, the fine grain qualities are not attained.

A distinctive characteristic of this treatment is that only a small amount of the oxide is used, and this is such that analysis of the finished steel shows that the quantity added is no longer existent and that the quantity present is not greater than 0.03% and, desirably, is less than 0.018%, e. g. cerium. This indicates that it is not the presence of an alloy which confers this fine grain property but rather an effect which is considered to induce nucleation.

It may be added, somewhat by way of recapitulation, that a steel, and particularly certain stainless varieties, having a tendency to solidify in large dendrites has a much smaller grain size as-cast than the untreated metal. This finer grain size improves the rolling qualities, increases resistance to corrosion, and gives a relatively high impact value at low temperatures.

It will be understood that the expression "rare earth oxide" as used in the subjoined claims includes the silicide, and other suitable compounds as carbonate and chloride, and also mixtures of oxides and/or silicides, and/or other compounds.

Since certain changes in carrying out the above process, and certain modifications in the product which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A method for the production of iron and steel which comprises preparing an iron containing melt, adding metallics thereto during furnacing, deoxidizing, incorporating a composition containing a rare earth oxide, then pouring and quick freezing.

2. A method for the production of iron and steel which comprises preparing an iron containing melt, adding metallics thereto during fur-

nacing, deoxidizing with the addition, and in conjunction therewith, of a composition containing a rare earth oxide, then pouring and quick freezing.

3. A method for the production of iron and steel which comprises preparing an iron containing melt, adding metallics thereto during furnacing, deoxidizing, incorporating a composition containing a plurality of rare earth oxides, then pouring and quick freezing.

4. A method for the production of iron and steel which comprises preparing an iron containing melt, adding metallics thereto during furnacing, deoxidizing with the addition, and in conjunction therewith, of a composition containing a plurality of rare earth oxides, said composition containing cerium oxide in a preponderant amount, then pouring and quick freezing.

5. A method for the production of iron and steel which comprises preparing an iron containing melt, adding metallics thereto during furnacing, deoxidizing substantially completely, then adding a composition containing a plurality of rare earth oxides, said composition containing cerium oxide in a preponderant amount, and being added in an amount not more than four pounds per ton, then pouring and quick freezing.

6. A method for the production of iron and steel which comprises preparing an iron containing melt, adding metallics thereto during furnacing, deoxidizing, adding a composition containing a rare earth oxide to the ladle, then pouring and quick freezing.

7. A method for the production of iron and steel which comprises preparing an iron containing melt, adding metallics thereto during furnacing, introducing a composition containing a rare earth oxide into the ladle, covering said oxide with a deoxidizing composition, and then pouring and quick freezing.

8. A method for the production of iron and steel which comprises preparing an iron containing melt, adding metallics containing chromium, molybdenum, manganese, nickel, and silicon thereto during furnacing, deoxidizing, adding a composition containing a rare earth oxide to the ladle in an amount not more than four pounds per ton, then pouring and quick freezing.

9. A method for the production of iron and steel which comprises preparing an iron containing melt, adding metallics containing chromium, molybdenum, manganese, nickel and silicon thereto during furnacing, deoxidizing, adding a composition containing a rare earth oxide to the ladle during pouring, and while the ladle is less than one-half full in an amount not more than four pounds per ton, then pouring and quick freezing.

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