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3,020,153

IRON AND STEEL PRODUCTION

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8 Claims. (Cl. 75-129)

The invention relates to a method for the production of rimming steels and includes correlated improvements and discoveries whereby the properties of rimming steels are decidedly improved.

Further, the procedure may be employed with particular advantage in rimming steels of alloy or of carbon grades, and the steels 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 a rimming steel may be produced as a fine grain product, markedly clean, and having distinctive corrosion and oxidation resistance.

Another object of the invention is to provide a process for the manufacture of a steel having a relatively lowered sulphur content, and with respect to which uneven distribution of the nitrogen and the hydrogen content may be materially avoided.

A particular object of the invention is the provision of a method whereby the foregoing are achieved, and a rimming steel of enhanced properties, is obtained through the utilization of a complex compound containing a single or a plurality of rare earth metals.

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

More especially the procedure comprises preparing an iron containing melt, adding metallics thereto which may contain a member of the group consisting of alloying elements chromium, manganese, molybdenum, nickel, tungsten, columbium, cobalt, tantalum, titanium, zirconium, boron and silicon during furnacing, with the addition when the iron or steel is ready, suitably to the ladle or to the ingot mold, of a complex rare earth metal salt which may be NaRF_4 in which R has the same meaning as hereinabove stated. If desired the melt may be deoxidized through the utilization for example of ferrosilicon, calcium silicon, ferromanganese and the like.

The addition of the complex rare earth metal salt 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 and desirably before the ladle is half full, that is, while the ladle is less than half full. Further, the complex rare earth metal salt may be added to the ingot mold or partly to the ladle and partly to the ingot mold. Moreover, we have found that when from about 0.5 to about 5 pounds of the complex rare earth metal salt have been added per ton of steel a very fine grain structure results attended by distinct cleanliness and uniformity and resulting in a product which has outstanding physical and working qualities and properties.

We have further found that depending on the pouring temperature, the size of the mold and the analysis of the iron or steel desired, an amount of about 2 pounds of a complex rare earth metal salt to the ton has accorded beneficial results. In the manufacture of the various steels the usual accepted good practice is employed and when the complex rare earth metal fluoride is added to the ladle, the steel may be poured at a temperature which

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has been found to be lower than usual practice due apparently to the fact that the treatment with the complex rare earth metal fluoride increases the fluidity of the treated metal. Varying quantities of the complex rare earth metal fluorides have been tried and found to be effective, for different conditions.

The procedure described herein makes effective use of the rare earth metal through the medium of the complex rare earth metal fluorides and at the same time utilizes a relatively small amount. It has been our definite finding that not more than 5 pounds per ton of the complex rare earth metal fluoride need be used provided that it is added as herein described and more particularly partly to the ladle and partly to the ingot mold.

For rimming steels, for example, the use of the complex rare earth metal fluoride effects a reduction of the nitrogen to about 0.003% and less without interfering with the rimming action. A sulphur reduction also takes place. A markedly clean steel results from the use of the complex rare earth metal fluoride and it possesses the desired physical properties.

Rimming steels which are known as effervescent steels are ones in which the CO gas is not eliminated and as a result it continues action so long as the steel is liquid and when it is poured into a mold the steel that freezes adjacent or close to the wall of the mold forces the carbon monoxide gas out of it and, as the freezing process continues, a rim of solid metal is made and the center of this steel which is liquid until the last continues to effervesce as the steel completely freezes, leaving a somewhat porous material in the middle. Also, in the middle of this steel are entrapped most of the inclusions, non-metallics and occluded gases. In these occluded gases is found nitrogen in quantities sufficient that when the steel is rolled out into a finished bar or sheet the material after a short period of time will start to warp or curl, caused by the strain induced by these nitrides.

It has been desired for many years to make a steel which would be rimming and non-aging inasmuch as it would give a much better surface and would require less conditioning. According to the present invention there may be added to a rimming steel a complex rare earth metal fluoride, for example NaRF_4 in which R represents a single or a plurality of rare earth metals which salt is characterized by the physical property of dissociation whereupon the dissociated products act in manners which are highly beneficial to rimming steels.

As above indicated, we have been able to reduce the nitrogen content to 0.003% and less and the sulphur content has been lowered by as much as 0.008 or 0.014%. There is not any deleterious action on the rimming mechanism and hence the reduction of sulphur which leads to the production of much cleaner steel, we are able to produce a non-aging steel which is not only non-aging but is of unique cleanliness.

The cleanliness of the steel has been shown by deep etch and by microscopic examination. Moreover, there is a large reduction in the formation of inclusions between the rim and the core with both the rim and the core showing the steel to be of a dense structure and clean.

Furthermore, the utilization of the complex rare earth metal fluorides does not alter the regular practice for the manufacture of rimming steels and we have found that it is sometimes advantageous to introduce about 75% of the complex rare earth metal fluoride into the ladle and about 25% into the ingot mold, and satisfactory results have been obtained by introducing all of the complex salt into the ingot mold. This is deemed to obviate reabsorption of gases into the steel when it is poured from the ladle into the ingot mold.

As an illustrative embodiment of a manner in which the

invention may be practiced, the following example is presented:

Example

A heat of manganese steel was made according to the following specification expressed in percentages:

Carbon	0.06-0.10.
Manganese	.20-.40.
Silicon	0.01 maximum.
Sulfur	0.03 maximum.
Phosphorus	0.01 maximum.

The charge consisted of:

	Lbs.
Limestone	18,500
Iron ore	58,000
Scrap	123,600
Hot metal	328,000

After the melt had been formed and after furnacing there were added:

	Lbs.
Burned lime	8,500
Iron ore	22,000

To the ladle at the tap there were added:

	Lbs.
Ferromanganese (85% manganese)	3,000
Aluminum	90

To the ingot mold there were added:

Aluminum	ozs.	15
Complex rare earth metal salt	lbs.	20

The steel from the ladle had the following analysis expressed as percentages:

Carbon	0.08.	35
Manganese	0.3.	
Silicon	0.006.	
Phosphorus	0.007.	
Sulfur	0.022.	
Iron	the remainder.	40

We have also found that the melt, after treatment in the ladle, sometimes advantageously may 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. Furthermore, when molten ferrous metal has been treated as herein described a fine grain results and later certain definite physical and chemical characteristics are attained. Additionally, it is highly desirable to make the steel so that this fine grain as-cast persists. This may in some cases be accomplished by casting at relatively low temperature and tapping or teeming as quickly as possible to solidify the iron or steel.

Preparation of the complex rare earth metal fluorides may be effected by first producing a halide and then fusing it, for example, with sodium fluoride suitably at an elevated temperature of about 1300° to about 1400° C.

The complex rare earth metal fluorides, for example, may be prepared from rare earth metal chlorides by converting the chlorides to the fluorides, and then fusing the fluoride with NaF. The chlorides are dissolved in water and filtered to remove insoluble impurities. The chloride filtrate is combined with a solution of NaF, and a pink-white precipitate forms. This precipitate is removed by filtration and washed until free of chloride. The rare earth metal fluorides are dried; 1 part thereof mixed with about 4 parts of solid NaF, and fused at about 1300° to about 1400° C. Excess NaF is removed by repeated washings with boiling water and the remaining product dried, and/or fused.

More particularly, two hundred grams of a natural mixture of rare earth metal chlorides were dissolved in 1000 ml. of water and the solution filtered to remove insoluble material. 50 ml. of hydrochloric acid, about 30%, were added to aid the filtering operation. A saturated solution of sodium fluoride was then added to the solu-

tion of rare earth metal chlorides until precipitation of fluorides was complete. The precipitate was removed by filtration, washed with hot distilled water until free from chlorides, dried at 110° C., and ground to 200 mesh. 102.23 grams of rare earth metal fluorides were thus obtained.

Sixty-five and thirty-four one hundredths grams of sodium fluoride were thoroughly mixed with the rare earth metal fluorides in the molar ratio of 1 to 3, and the mixture was fused in a platinum crucible placed in a Globar furnace for 60 minutes. The starting temperature in the furnace was 1250° C. and the final temperature was 1285° C. After fusing, the product was cooled to room temperature. The product was ground and washed with hot distilled water to remove excess sodium fluoride. The solids were separated by centrifuging and siphoning the clear liquid. The washed product was dried and ground.

Other methods of producing the complex rare earth metal fluorides are useable; such as direct fluoridization, and fusion.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in carrying out the above method and in the composition set forth without departing from the scope of the invention, 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 rimming steels which comprises preparing an iron containing melt, adding a metallic containing material during furnacing, incorporating from 0.5 to 5.0 pounds per ton of iron of a complex rare earth metal salt therewith said salt having the general formula MRX_4 in which M represents a member of the group consisting of sodium and potassium, R represents a rare earth metal having an atomic number ranging from 57-71, and X is fluorine.

2. A method for the production of rimming steels as defined in claim 1 in which M is sodium.

3. A method for the production of rimming steels which comprises preparing an iron containing melt, adding a metallic containing material during furnacing, incorporating from 0.5 to 5.0 pounds per ton of iron of a complex rare earth metal salt therewith said salt having the general formula MRX_4 in which M represents a member of the group consisting of sodium and potassium, R represents a plurality of rare earth metals having an atomic number ranging from 57-71, and X is fluorine.

4. A method for the production of rimming steels as defined in claim 3 in which M is sodium.

5. A method for the production of rimming steels which comprises preparing an iron containing melt, adding a metal selected from the group consisting of chromium, manganese, molybdenum, nickel, tungsten, columbium, cobalt, tantalum, titanium, zirconium, boron and silicon thereto during furnacing, and incorporating from 0.5 to 5.0 pounds per ton of iron of a complex rare earth metal salt therewith having the general formula MRX_4 in which M represents sodium, R represents a plurality of rare earth metals having an atomic number ranging from 57-71, and X is fluorine.

6. A method for the production of rimming steels which comprises preparing an iron containing melt and incorporating from 0.5 to 5.0 pounds per ton of iron of a complex rare earth metals salt therewith, said salt having the general formula MRX_4 in which M represents

sodium, R represents a rare earth metal having an atomic number ranging from 57 to 71, and X is fluorine.

7. A method as claimed in claim 6 in which the complex rare earth metal salt is added to the ladle.

8. A method as claimed in claim 6 in which the complex rare earth metal salt is added to the ingot mold.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,020,153

February 6, 1962

Arthur Linz et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the grant, lines 1 and 2, for "Arthur Linz, of New York, N. Y., and Norman F. Tisdale, of Pittsburgh, Pennsylvania," read -- Arthur Linz, of New York, N. Y., and Norman F. Tisdale, of Pittsburgh, Pennsylvania, assignors to Molybdenum Corporation of America, of New York, N. Y., a corporation of Delaware, --; line 11, for "Arthur Linz and Norman F. Tisdale, their heirs" read -- Molybdenum Corporation of America, its successors --; in the heading to the printed specification, lines 3 and 4, for "Arthur Linz, 35 E. 35th St., New York, N. Y., and Norman F. Tisdale, 1408 Navahoe Drive, Pittsburgh, Pa." read -- Arthur Linz, New York, N. Y., and Norman F. Tisdale, Pittsburgh, Pa., assignors to Molybdenum Corporation of America, New York, N. Y., a corporation of Delaware --; column 3, line 30, for "15" read -- 16 --.

Signed and sealed this 31st day of July 1962.

(SEAL)

Attest:

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Commissioner of Patents