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STAINLESS STEEL AND METHOD OF PRODUCTION

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The invention relates to a method for the production of stainless steels and to the products obtained thereby, 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, 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 a stainless steel may be produced as a fine grain product, and having distinctive corrosion and oxidation resistance and high impact values at room and at low temperatures.

Another object of the invention is to provide a process for the manufacture of a stainless steel having a relatively lowered sulphur content.

A particular object of the invention is the provision of a method whereby the foregoing are achieved, and a product, namely a stainless steel of enhanced properties, is obtained through the utilization of a composition containing a rare earth metal, preferably a plurality of rare earth metals with cerium being present in a preponderant amount.

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, 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, cobalt, titanium, tantalum, columbium and zirconium with varying amounts of silicon, 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, reduce the opportunity for corrosive and oxidation agents to attack the steel.

In view of the fact that the alloys which are usually employed in producing stainless steels are in great demand and as such are hard to obtain at all times, we decided to attempt to improve these types by producing a fine grain in

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the steel and to do this the molten steel has been treated with an alloy which is made up essentially of metals 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 stainless 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 stainless steels, such as the high alloy types, as austenitic; the chrome type e. g. 19% chromium, and certain 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 composition containing a rare earth metal, either singly or in compatible combination, and suitably that which is now known in the trade, and which we designate herein as "L-metal" which contains a mixture of rare earth metals, and desirably containing a preponderant amount of cerium, of the following approximate percentage composition, cerium 50.00, lanthanum 30.00 and the balance various rare earth metals as praseodynium, samarium, neodymium, etc., and iron to a melt, that is to the liquid steel.

More especially, the procedure comprises preparing an iron containing melt, adding metallics, e. g. a member of the group consisting of chromium, manganese, molybdenum, nickel, columbium, titanium, tantalum, cobalt, zirconium and silicon, thereto during furnacing, deoxidizing, utilizing e. g. ferro silicon, calcium silicon, ferro manganese, and the like, and then adding the composition which, more particularly, contains a plurality of rare earth metals having cerium present in a preponderant amount.

While the addition of the rare earth metal may be effected at different phases of the melting and furnacing, a suitable procedure is to add it to the ladle either before 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, another and somewhat preferred procedure is to place the material 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 ferrous metal may be poured on top of it. Either method delays the action of the "L-metal" so that there will be

sufficient liquid metal to allow a proper reaction therewith.

Further, we have found that when not more than about 3 pounds of the "L-metal," or its equivalent, have been added per ton of the 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 pound of the "L-metal" to the ton has given beneficial results.

Stainless steels, which sometimes are 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 metal, 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, the usual accepted good practice is employed and in addition to it, care is taken to see that the melt is properly deoxidized, that is, 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 metal seemingly increases the fluidity of the treated metal.

Various quantities of rare earth metal have been tried and found to be effective. However, when excessive amounts of the metal have been added, the product has been found to be extremely dirty and as such offered low resistance to oxidation or corrosion. Our method makes efficient use of the "L-metal" and at the same time utilizes only a very small amount. We have definitely found that not more than three pounds of "L-metal" per ton need to 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 heat was made having the following analysis expressed as percentages:

Carbon	0.06
Manganese	1.75
Phosphorus	0.02
Sulphur	0.009
Silicon	0.6
Nickel	20.2
Chromium	24.5
Rare earth metal	0.005

Remainder iron.

The charge consisted of:

	Pounds
Scrap (18–8)	6,000
Scrap (24–20)	8,000
Scale	4,000

The power having been turned on, the following additions were made:

	Pounds
Burnt lime	800
Chromium silicide	800
Limestone	300
Ferro silicon (75% Si)	200

When the charge had been melted, 4500 pounds of ferro chrome, having not more than 0.06 carbon, were added to the furnace as were also 100 pounds of 75% ferro silicon, with an additional 50 pounds being added to the slag. When the chrome addition was melted, 1400 pounds of nickel in the form of nickel plate and 300 pounds of low carbon manganese were introduced.

Following adequate working of the heat, and the slag being in proper condition, approximately seven hours from charge to pour; 30 pounds of "L-metal," that is a mixture of rare earth metals that may consist preponderantly of cerium, were added to the ladle, and covered with 150 pounds of calcium silicide (62% Si). The slag was held back and the heat was tapped in approximately two minutes. Pouring temperature was about 2750° F. and a slight reaction when the ladle was full indicated that all of the "L-metal" had not been absorbed into the liquid steel.

The ingots were allowed to stand for one hour, after which they were stripped and placed in soaking pits. After approximately 12 hours therein, the ingots were rolled to a strip mill billet size 14¼" x 3¼" from a 20½" round ingot. A thorough examination disclosed that there were no cracked edges.

A determination of the sulphur content showed that there was a decrease of about 0.01% by the addition of the "L-metal." This was demonstrated by samples taken before and after the "L-metal" was added. Similar heats were made to establish the reduction of sulphur content both in small induction type furnaces and in large furnaces. In each case it was clearly demonstrated that the introduction of the rare earth metal effected a reduction of the sulphur content.

EXAMPLE 2

A heat was made having the following analysis expressed in percentages:

Carbon	0.1
Manganese	2.24
Phosphorus	0.026
Sulphur	0.012
Silicon	0.63
Nickel	19.0
Chromium	24.0
Rare earth metal	0.005

Remainder iron.

The charge consisted of:

	Pounds
Pig iron	1,000
Scrap (18–8)	29,000
Sheet nickel (Hi Ni)	6,000

After the charge had been melted and during furnacing, there were added:

	Pounds
Ferro chromium (0.1 C)	11,500
Ferro chromium (68% Cr)	350
Ferro silicon (75% FeSi)	650
Ferro manganese (82% Mn)	850
Sheet nickel	1,700

To the ladle, prior to or during pouring, and suitably when about one-fourth full, there were added calcium silicide 300 pounds and "L-metal" 75 pounds.

The method herein described for the production of stainless steels leads to the formation of a fine grain structure which enhances the resistance to corrosion. Since there is only a small amount of the "L-metal" 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 "L-metal" 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 the 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 "L-metal," are a reduction of the sulphur content and the obtention of a fine grain as cast. These occasion higher impact values at lower temperatures, and 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 "L-metal," or a metal made from a combination of rare earths, 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, e. g. at temperatures from about 2710° F. to 2780° F. 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 metal compares in almost every way, with untreated metal. Thus, when a melt is treated with "L-metal" 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 rare earth metal 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 0.018%, 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.

Metallurgical examination of the results of the treatment of liquid ferrous material with "L-metal" leads to the belief either that the "L-metal" is oxidized, or that it forms a compound with some of the non-metallics or with

occluded gases which offer nuclei for crystallization similar to the result of adding titanium to aluminum, whereby a fine grain is obtained.

The following tabulation evidences the marked resistance to corrosion and oxidation of steels produced in accordance with the method herein described.

Stainless Steel
Corrosion and Oxidation Tests

Type	Scale Resistance		10% H_2SO_4 gram loss in 1 mo.	10% HCl gram loss in 1 mo.
	1,900° F. grms/sq. in.	2,100° F. grms/sq.in.		
310	.034	.01	.017	.357
310—Ce	.017	.005	.004	.031

The 310 type contains about 25% chromium and about 20% nickel. Further the rare earth metal content, expressed as cerium, desirably may range from about 0.003% to about 0.009%, and suitably will be about 0.005%.

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

Furthermore the addition, as above indicated, of a rare earth metal either singly or in compatible admixture effects a reduction in the sulphur content, and such reduction results in enhanced physical properties and distinctive cleanliness in the product.

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 a stainless steel which comprises preparing an iron containing melt, adding metallics including a member of the group consisting of chromium, molybdenum, manganese, nickel, columbium, titanium, tantalum, cobalt, zirconium and silicon thereto during furnacing, deoxidizing, incorporating a composition containing a rare earth metal, in an amount not more than three pounds per ton, pouring and quick freezing.

2. A method for the production of a stainless steel which comprises preparing an iron containing melt, adding metallics including a member of the group consisting of chromium, molybdenum, manganese, nickel, columbium, titanium, tantalum, cobalt, zirconium and silicon thereto during furnacing, deoxidizing with the addition, and in conjunction therewith, of a composition containing a rare earth metal, in an amount not more than three pounds per ton, pouring and quick freezing.

3. A method for the production of a stainless steel which comprises preparing an iron containing melt, adding metallics including a member of

the group consisting of chromium, molybdenum, manganese, nickel, columbium, titanium, tantalum, cobalt, zirconium and silicon thereto during furnacing, deoxidizing, incorporating a composition containing a plurality of rare earth metals, in an amount not more than three pounds per ton, pouring and quick freezing.

4. A method for the production of a stainless steel which comprises preparing an iron containing melt, adding metallics including a member of the group consisting of chromium, molybdenum, manganese, nickel, columbium, titanium, tantalum, cobalt, zirconium and silicon thereto during furnacing, deoxidizing with the addition, and in conjunction therewith, of a composition containing a plurality of rare earth metals, said composition containing cerium in a preponderant amount, in an amount not more than three pounds per ton, pouring and quick freezing.

5. A method for the production of a stainless steel which comprises preparing an iron containing melt, adding metallics including a member of the group consisting of chromium, molybdenum, manganese, nickel, columbium, titanium, tantalum, cobalt, zirconium and silicon thereto during furnacing, deoxidizing substantially completely, then adding a composition containing a plurality of rare earth metals, said composition containing cerium in a preponderant amount, and being added in an amount not more than three pounds per ton, pouring and quick freezing.

6. A method for the production of a stainless steel which comprises preparing an iron containing melt, adding metallics including a member of the group consisting of chromium, molybdenum, manganese, nickel, columbium, titanium, tantalum, cobalt, zirconium and silicon thereto during furnacing, deoxidizing, adding a composition containing a rare earth metal to the ladle in an amount not more than three pounds per ton, pouring and quick freezing.

7. A method for the production of a stainless steel which comprises preparing an iron containing melt, adding metallics including a member of the group consisting of chromium, molybdenum, manganese, nickel, columbium, titanium, tantalum, cobalt, zirconium and silicon thereto during furnacing, deoxidizing, adding a composition containing a rare earth metal to the ladle during tapping and while the ladle is less than one-half full, in an amount not more than three pounds per ton, pouring and quick freezing.

8. A stainless steel characterized by a fine grain structure, substantial freedom from dendrites, resistance to corrosion, a relatively high impact value at low temperatures, capable of being directly rolled to billet size, containing the following and substantially of the composition expressed as percentages: carbon 0.06–0.1, manganese 1.75–2.24, phosphorus 0.02–0.026, sulphur 0.009–0.012, silicon 0.60–0.63, nickel 19.0–20.2, chromium 24.0–24.5, rare earth metal 0.003–0.009, and the remainder iron, said steel being produced by the method defined in claim 1.

9. A stainless steel characterized by a fine grain structure, substantial freedom from dendrites, resistance to corrosion, a relatively high impact value at low temperatures, capable of being directly rolled to billet size, containing the following and substantially of the composition expressed as percentages: carbon 0.06–0.1, manganese 1.75–2.24, phosphorus 0.02–0.026, sulphur 0.009–0.012, silicon 0.60–0.63, nickel 19.0–20.2, chromium 24.0–24.5, rare earth metal about 0.005, and the remainder iron, said steel being produced by the method defined in claim 1.

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