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METHOD FOR PRODUCING NON-AGING RIMMED STEELS

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This invention relates to a method for the preparation of non-aging rimmed steels.

The problem of producing a deep-drawing steel stabilized against age-hardening effects has been consistently high on the list of problems dealt with by industry. It has been long recognized that nitrogen is the principal element which causes the age-hardening phenomenon in steel. At the present time, most of the steels produced for deep-drawing applications are treated in the molten stage by the addition of strong deoxidizers such as aluminum, titanium, or zirconium. These elements are added in precise and predetermined amounts to effect complete deoxidation and produce what is known in the industry as a "killed" steel. In these steels, aluminum is most commonly used to completely deoxidize the steel and at the same time precipitate the nitrogen in the form of aluminum nitrides, thereby preventing the nitrogen from dissolving in the alpha iron to eventually precipitate as iron nitride. As opposed to iron nitride, which precipitates at room temperature and thus may alter the properties of the steel when stored, nitrides of aluminum, titanium, and zirconium precipitate at relatively high temperatures so that essentially all of the nitrogen is tied up by the time the ingot is cool. Thus, once the metal is fabricated, no significant amount of aging can occur due to the nitrogen effect even though it is stored for extended lengths of time. The disadvantages of aluminum-killed steels are the relatively low yields due to hot-top losses and a tendency toward erratic surface quality due to entrapment of alumina at or near the surface.

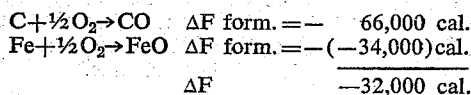
The disadvantages inherent in killed steels are not present in rimmed steels. In the preparation of rimmed steel, as a result of the reaction between oxygen and carbon while the metal is solidifying in the ingot, the molten metal effervesces, giving off a large volume of carbon monoxide, and forming deep-seated blow holes in the final ingot which are eliminated during hot working. This eliminates the need for hot-topping, and, in general, considerably less loss of metal is incurred with rimmed steel ingots than with killed steels since less cropping is necessary. In rimmed steels, however, the nitrogen is in solution in the ferrite and it is believed that during storage unstable iron nitrides form and aging results. Aging is manifested by increased strength and hardness, by decreasing toughness and ductility, and, in some cases, by the return of a distinct yield point in cold-worked material.

It has been proposed that non-aging rimmed steels be prepared by adding selected nitride forming elements while the steel is in the molten state. The nitride-former, however, must not have such superior deoxidizing properties as to cause the steel to be killed. Production of a non-aging rimmed steel, therefore, depends upon the addition of a nitride-forming element which does not appreciably inhibit the rimming action. Workable additives may be selected by using the rimming reaction $\text{FeO} + \text{C} \rightarrow \text{CO} + \text{Fe}$ as the standard.

The free energy change (ΔF) of the reaction of this equation is the sum of the free energy change of the for-

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mation of the products of the reaction minus the sum of the free energy change of formation of the reactants of the reaction. As applied to the carbon reduction of FeO at 1600°C . on a molar basis, the following has been thermodynamically established:



If the free energy change of the reaction between the added element or elements with the iron oxide is more negative than $-32,000$ calories per mole, the rimming action will be inhibited to a great extent, or completely stopped if the affinity of the element for oxygen is excessively high. Under such conditions, a killed steel would result. Conversely, if the free energy change of the reaction is less negative than $-32,000$ calories per mole, the rimming action would proceed and a non-aging rimmed steel would be produced. The four elements listed below have nitride-forming tendencies and, when reacting with iron oxide, have a free energy change reaction less negative than that produced by the carbon reduction of iron oxide to form carbon monoxide:

Columbium
Tantalum
Vanadium
Boron

Other elements are available as nitride-formers which meet the requirements outlined above, such as silicon and chromium, but these are not feasible either for economic or technical reasons.

Various experimenters have heretofore attempted to produce non-aging rimmed steels by the addition of elemental vanadium or boron. These attempts have failed to meet with success. Vanadium behaves erratically in stabilizing nitrogen and, since recoveries of the metal are poor, it is also expensive to use. The use of boron alone involves very critical control due to the small amount required to achieve non-aging characteristics. Certain other of the above additives, especially those of low specific gravity, have low recoveries attributable primarily to air oxidation as a result of their tendencies to stay on the surface of the molten metal for extended periods of time. In many cases as well, poor uniformity of distribution results, especially when the metal is added in unalloyed, elemental form or in small quantities.

It is, therefore, the primary object of this invention to provide an improved method for the preparation of non-aging rimmed steels.

Other objects are to provide such a method whereby columbium, tantalum, vanadium, and boron may be efficiently added to steel melts, singly or in combination, to provide such a non-aging rimmed steel.

The above objects are achieved by providing a molten bath of nitrogen-containing steel, adding to said molten bath an addition agent comprising at least 25 percent manganese and at least one element selected from the group consisting of columbium, tantalum, vanadium, and boron in an amount sufficient to combine with the free nitrogen in said steel.

An element which is known to be a good nitride-former, and is otherwise suitable for producing non-aging rimmed steels, may be added to steel more efficiently from a recovery and distribution viewpoint when such an element is alloyed with, or is present as a component in a bonded mixture with, manganese. Other physical proper-

ties such as wear resistance and a lowering of hardening temperature are also improved by the presence of this element. With respect to the present invention, however, manganese is essential because of its dual roles as diluent and distributor of difficult-to-handle reactive elements. The simultaneous addition of manganese is an important feature of the present invention and makes possible the attainment of more uniform distribution, decreased criticalness of additive amount, and better recoveries of the nitride-forming element. Since manganese is normally added in the ladle, the method of the invention will most commonly be carried out after the molten steel has been tapped into the ladle. Supplementary nitride-formers and/or deoxidizers, as well as other important alloying constituents, may be added at the same time.

Example I

As an example of the method of the invention, assume a steel having a manganese content in the open hearth between 0.10 and 0.12 percent by weight. Assume a desired final manganese content between 0.30 and 0.35 percent, and assume additionally that a normal 85 percent recovery of manganese will be achieved. For these conditions, the addition agents added in the practice of the method of the invention should add from approximately 4.2 to 5.9 pounds of manganese per ton of steel tapped. Next, assuming a nitrogen content of 0.004 percent (deep-drawing, open hearth steel usually contains between 0.003 and 0.005 percent nitrogen) in a steel whose base composition is 0.07 percent carbon, 0.35 percent manganese, 0.01 percent silicon, 0.03 percent maximum phosphorus, and 0.04 percent maximum sulfur, any nitride-forming element or combination of elements must be added to a level of 0.0159 atomic percent (0.004 percent by weight nitrogen $\div$ 0.0159 atomic percent nitrogen) times the ratio of the atoms of nitride-forming element to nitrogen atoms in the stable nitride that is formed.

Conversions may, therefore, be made on the four nitride-formers referred to above, to the following weight percentages, based on the steel composition of the example and a nitrogen content of 0.004 weight percent.

Nitride-Former	Nitride-Formed	Weight Percent
Columbium.....	CbN.....	0.0264
Tantalum.....	TaN.....	0.0517
Vanadium.....	VN.....	0.0146
Boron.....	BN.....	0.0031

The weight percent figures in the above table are derived by multiplying a conversion factor which, on the basis of the nitrogen content of the steel, is equal to 0.000283, by the atomic weight of the element in question.

The calculated amounts given, however, are not those actually used in the practice of the invention. For example, at least twice as much vanadium is required to produce a non-aging steel. This additional quantity is necessary as the excess combines with oxygen, sulfur, and carbon, to form inclusions or dissolve in the steel. A quantity in excess of that which unites chemically with other constituents in the steel is required to be present for forming nitrides. Using the above weight percentages and knowing the oxide-, carbide- and sulfide-forming tendencies of the elements in question, it is, therefore, possible to provide approximate multiplication factors for each of the elements as is done in the following table. Also indicated in this table are the expected recoveries of each element to account for losses of the addition agent components to the slag or those attributed specifically to volatilization of the additive constituents. The extreme right-hand column, therefore, gives the total amount of the nitride-forming element that should exist in the manganese-base addition agent if only one such element is

added and if nitrogen is present in an amount approximating 0.004 percent by weight:

Nitride-Former	Theoretical Addition, Weight Percent	Multiplication Factor	Expected Recovery, Percent	Element Required in Addition, Lb./Ton
Columbium.....	0.026	2	75	1.52
Tantalum.....	0.052	2	75	2.84
Vanadium.....	0.015	2	75	0.8
Boron.....	0.003	1.5	75	0.12

It is to be understood that the manganese content of the addition agent may be derived from any source. For example, elemental manganese or ferromanganese may be used with equally satisfactory results. Similarly, the sources of the nitride-forming elements are equally varied. These elements may be incorporated with the manganese in their elemental states or as alloys. Ferrovandium may be combined with ferromanganese to form an addition agent for use in practicing the method of the invention, for example.

If the nitride-formers listed above are added individually in their elemental states to medium carbon ferromanganese comprising 80.0 percent manganese, the addition agents of the example would have the following composition:

Element	Manganese, Percent	Nitride-Former, Percent	Iron, Percent
Columbium.....	67	17	Bal.
Tantalum.....	58	30	Bal.
Vanadium.....	72	10	Bal.
Boron.....	79	1.72	Bal.

The above example has illustrated the manner in which addition agents may be composed for practicing the method of the invention with a specific steel containing 0.004 percent nitrogen and requiring a manganese addition of approximately 5.5 pounds per ton. If the steel composition varies from that assumed in Example I, the addition agent may be varied accordingly.

Example II

Assume a steel having the same manganese requirements as that of Example I. Assume nitrogen contents of 0.002 and 0.005 percent for purposes of calculation. The weight percent requirements of each element are as follows:

Nitride-Former	Weight, Percent	
	0.002 N ₂	0.005 N ₂
Columbium.....	0.0132	0.0330
Tantalum.....	0.0258	0.0647
Vanadium.....	0.0073	0.0182
Boron.....	0.0015	0.0039

The total requirements of each element, taking into account the same multiplication factors and expected recovery percentages used in Example I are as follows:

Nitride-Former	Theoretical Addition, Weight Percent	Multiplication Factor	Expected Recovery, Percent	Element Required in Addition Lb./Ton
Columbium.....	0.013	2	75	1.04
Tantalum.....	0.033	2	75	1.74
Vanadium.....	0.026	2	75	1.39
Vanadium.....	0.065	2	75	3.48
Vanadium.....	0.007	2	75	0.38
Vanadium.....	0.018	2	75	0.96
Boron.....	0.001	1.5	75	0.04
Boron.....	0.004	1.5	75	0.16

It should be understood, however, that the steel heat at times may contain more than 0.10 to 0.12 percent manganese. In such cases, and also where it is desirable to add part of the manganese as a separate addition, less manganese than that prescribed above may be added. When this is the case, the same amount of nitride-former will represent a greater percentage of the total addition agent. The ranges given in the last table of Example II might then be increased as follows:

Element	Manganese, Percent	Nitride-Former, Percent	Iron, Percent
Columbium	40-75	15-30	Bal.
Tantalum	30-65	25-40	Bal.
Vanadium	45-80	5-20	Bal.
Boron	50-85	1-4	Bal.

Example III

An example is given here of a complexing calculation when it is desired to incorporate more than one nitride-former with manganese for use in the practice of the method of the invention. The steel is similar to that of Example I.

Assume that for economic reasons it is desired to use $\frac{2}{3}$ vanadium and $\frac{1}{3}$ boron.

Because there exists 0.0159 atomic percent nitrogen in the steel, there must exist an equal amount of effective nitride-formers.

$$\frac{2}{3} (.0159) = 0.0106 \text{ atomic percent vanadium;}$$

$$\frac{1}{3} (.0159) = 0.0053 \text{ atomic percent boron.}$$

Heat No.	Additive	Steel Composition Produced, Percent							
		Al	Mn	Si	C	N	Ti	V	B
1	Normal rimmed steel	0.014	0.25	0.01	0.052	0.004			
2	2-3% B in FeMn	0.005	0.54	0.03	0.15	0.002			0.007
3	40% V, 30% Mn, 7% Al, 10% Ti Alloy	0.013	0.34	0.02	0.09	0.005	0.01	0.046	
4	40% V, 30% Mn, 7% Al, 10% Ti bonded mixture	0.013	0.37	0.03	0.08	0.004	0.01	0.04	

Convert to weight percentages:

$$0.0106 = \frac{\frac{\text{wt. percent V}}{\text{at. wt. V}}}{1.80 + \frac{\text{wt. percent V}}{\text{at. wt. V}}}$$

$$\text{weight percent V} = 0.00973$$

$$0.0053 = \frac{\frac{\text{wt. percent B}}{\text{at. wt. B}}}{1.80 + \frac{\text{wt. percent B}}{\text{at. wt. B}}}$$

$$\text{weight percent B} = 0.00103$$

Using multiplication factors and expected recoveries, the following percentages of vanadium and boron must be added to the steel:

$$\text{Wt. percent V} = \frac{.0097(2)}{.75} = 0.026$$

$$\text{Wt. percent B} = \frac{.001(1.5)}{.75} = 0.00206$$

On a per ton basis, the following is required: 0.52 lb. V; 0.04 lb. B.

If ferromanganese containing 82 percent manganese is utilized in order to add 5.5 pounds of manganese per ton of steel, the final addition agent will have the following composition:

76 percent Mn
7.2 percent V
0.55 percent B

Complexing to the extent of incorporating other elements than nitride-formers may be advantageous from still another point of view. For example, small amounts

of elements that are primarily deoxidizers and only secondarily nitride-formers may be complexed with the primary nitride-formers. Elements falling into this category might include zirconium, titanium, beryllium, magnesium, aluminum, calcium, silicon and/or barium. Since even the nitride-formers oxidize to varying extents, these reactive elements would preferentially deoxidize and desulfurize and thus increase the amount of the main nitride-former that would be available for tying up the nitrogen. This practice would also increase the recovery of the main element, and, therefore, a lesser addition of this element would be required. It is proposed, therefore, that the more reactive elements may be added to any of the manganese-base addition agents in an amount up to 12.5 percent. The total amount of each nitride-former is not affected by such addition although, of course, its percentage amount in the addition agent is thereby decreased.

The inclusion of manganese as a major constituent of the addition agents used in the practice of the invention serves to effectively distribute the nitride-forming elements in the melt whereby better control may be achieved. Best results are obtained if manganese is present in the addition agent in the amount of at least 25.0 percent.

As examples of the effectiveness of the method of the invention, the following steel heats were produced utilizing as addition agents a ferromanganese-boron alloy, and a manganese-vanadium-aluminum-titanium combination, the latter being produced both as an alloy and as a "Sol"-type product, that is, a bonded mechanical mixture.

Heat No. 1 was included as a base heat for the sole purpose of comparison. Heat No. 2 shows the results of utilizing a boron addition with manganese as the carrier and heats 3 and 4 show the results of vanadium additions, with manganese in the low range, where minor amounts of primary deoxidizers are employed in combination with the nitride-former.

When tested at different temperatures for tensile strength, samples of the above steels yielded the following results:

Heat No.	Tensile Strength, p.s.i.		
	Room Temperature	At 400° F.	Change
1	45,400	62,500	+17,100
2	51,500	43,800	-7,700
3	52,200	43,900	-8,300
4	49,400	42,500	-6,900

To those skilled in the art, it is obvious that the decrease in tensile strength on specimens tested from room temperature to 400° F. shows that the steel produced by the addition agents of the invention have excellent non-aging properties. Thus, manganese may be added simultaneously and in intimate relationship with the nitride-formers, with or without deoxidizers, to produce non-aging rimmed steel.

When samples of the heats were prestrained to 7 per-

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cent elongation at room temperature and aged to 212° F. for 1 hour, the following results were obtained:

Heat No.	Aged 1 Hour at 212° F.		
	Stress at 7% Elong.	Yield Strength, p.s.i.	Aging Index
1	37,900	44,100	+6,200
2	43,900	44,700	+800
3	44,600	45,200	+600
4	42,700	44,300	+1,600

The above data further substantiates the excellence of heats produced using the method of the invention with respect to non-aging properties.

The manganese-base alloys or bonded mixtures of the invention thus represent highly useful addition agents for producing non-aging, rimmed steels. Such steels, because of their non-aging properties, may be stored for extended periods of time without fear of loss of formability or deep-drawing qualities due to nitrogen effect. Because the nitride-formers and deoxidizers are added in such amounts as not to interfere with the rimming action, ingots are produced which have good surface quality. In addition, manganese need not be added separately to bring the manganese content up to specification. The addition of complex addition agents also serves to produce better recoveries and more complete dispersion of the individual components of the alloys or bonded mixtures falling within the scope of the present invention.

As used in the appended claims, the term "major constituent" of manganese refers to an amount of manganese not less than 25 percent by weight of the addition agent.

Although the above description and examples have been primarily predicated upon the treatment of steel having 0.002 to 0.005 percent by weight nitrogen content, it is to be understood that the invention is not so limited. The addition of manganese base agents within the scope of this invention may be practiced with equal effectiveness in the treatment of steels to be utilized for deep-drawing applications having any nitrogen content.

What is claimed is:

1. A method for the production of non-aging rimmed steel which comprises providing a molten bath of steel, adding to said molten bath an addition agent comprising at least 25 percent manganese and at least one element selected from the group consisting of columbium, tantalum, vanadium, and boron in an amount sufficient to combine with the nitrogen in said steel.

2. A method for the production of non-aging rimmed steels which comprises providing a molten bath of steel, adding to said molten bath an addition agent comprising at least 25 percent manganese, at least one element selected from the group consisting of columbium, tantalum, vanadium, and boron in an amount sufficient to combine with the nitrogen in said steel, and up to 12.5 percent of an element selected from the group consisting of zirconium, titanium, beryllium, magnesium, aluminum, calcium, silicon, and barium.

3. A method for the production of non-aging rimmed steels which comprises providing a molten bath of steel, adding to said molten bath an addition agent comprising at least 25 percent manganese, at least one element selected from the group consisting of columbium, tantalum, vanadium, and boron in an amount sufficient to combine with the nitrogen in said steel, up to 12.5 percent of an element selected from the group consisting of zirconium, titanium, beryllium, magnesium, aluminum, calcium, silicon, and barium, and the balance substantially all iron.

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4. A method for the production of non-aging rimmed steel which comprises providing a molten bath of steel, adding to said molten bath an addition agent comprising at least 25 percent manganese and up to a maximum of about 5.9 pounds of manganese per ton of steel, and 1.0 to 2.0 pounds columbium per ton of said steel.

5. A method for the production of non-aging rimmed steel which comprises providing a molten bath of steel, adding to said molten bath an addition agent comprising at least 25 percent manganese and up to a maximum of about 5.9 pounds of manganese per ton of steel, and 1.0 to 4.0 pounds of tantalum per ton of said steel.

6. A method for the production of non-aging rimmed steel which comprises providing a molten bath of steel, adding to said molten bath an addition agent comprising at least 25 percent manganese and up to a maximum of about 5.9 pounds of manganese per ton of steel, and 0.3 to 1.0 pound vanadium per ton of said steel.

7. A method for the production of non-aging rimmed steel which comprises providing a molten bath of steel, adding to said molten bath an addition agent comprising at least 25 percent manganese and up to a maximum of about 5.9 pounds of manganese per ton of steel, and 0.03 to 0.20 pound boron per ton of said steel.

8. A method for the production of non-aging rimmed steel which comprises providing a molten bath of steel, adding to said molten bath an addition agent comprising at least 25 percent manganese and up to a maximum of about 5.9 pounds of manganese per ton of steel, 1.0 to 2.0 pounds columbium per ton of said steel, and the balance substantially all iron.

9. A method for the production of non-aging rimmed steel which comprises providing a molten bath of steel, adding to said molten bath an addition agent comprising at least 25 percent manganese and up to a maximum of about 5.9 pounds of manganese per ton of steel, 1.0 to 4.0 pounds of tantalum per ton of said steel, and the balance substantially all iron.

10. A method for the production of non-aging rimmed steel which comprises providing a molten bath of steel, adding to said molten bath an addition agent comprising at least 25 percent manganese and up to a maximum of about 5.9 pounds of manganese per ton of steel, 0.3 to 1.0 pound vanadium, and the balance substantially all iron.

11. A method for the production of non-aging rimmed steel which comprises providing a molten bath of steel, adding to said molten bath an addition agent comprising at least 25 percent manganese and up to a maximum of about 5.9 pounds of manganese per ton of steel, 0.03 to 0.20 pound boron per ton of said steel, and the balance substantially all iron.

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