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PRODUCTION OF NITROGEN-BEARING STAINLESS STEEL

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This invention relates to stainless steel, more especially to an art of producing the same.

An object of my invention is the provision of an efficient, reliable and thoroughly practical process for producing nitrogen-containing stainless steel, which is readily executed with minimum departure from standard stainless steel metallurgical production operations and equipment.

A further object of my invention is the simple, efficient and economical production of stainless steels, of desirable physical properties made to a desired specification of iron, carbon, chromium and nitrogen, either with or without supplementary elements such as nickel, copper, manganese, cobalt, columbium, titanium, molybdenum, tantalum, tungsten, vanadium and the like.

A still further object of my invention is the production of inexpensive austenitic stainless steels wherein substantial quantities of nitrogen are employed as an austenite-forming ingredient.

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

The invention accordingly consists in the combination of elements, composition of ingredients and mixture of materials, and in the several steps and the relation of each of the same to one or more of the others as described herein, and the scope of the application of which is indicated in the following claims.

As conducive to a clearer understanding of certain features of my invention it may be noted at this point that the addition of a small percentage of nitrogen to stainless steel, as taught in the prior art, is known to lend many beneficial characteristics to the metal. In the straight chromium grades, the stainless steel containing nitrogen is of an inherently fine, even grain structure, this being particularly important in the high chromium grades; they are of improved workability over a wider range of working temperatures; they are less subject to grain growth, brittleness, decarburization and fatigue; and they are more durable and of high impact values than are similar stainless steels which contain only incidental quantities of nitrogen. In the chromium-nickel grades, the steels are rendered austenitic with much lower quantities of nickel, nitrogen acting as a substitute for nickel in whole or in part, thus effecting direct savings in this expensive alloying ingredient.

The successful and consistent production of

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nitrogen-bearing stainless steel, however, has heretofore presented a number of problems. Where nitrogen is introduced directly during the melting process, as by nitrogen gas or ammonia, the results are erratic. In some instances, a desired nitrogen content is achieved, in others it is not. No means are known for successfully and consistently adding desired amounts of nitrogen to molten stainless steel.

Where high nitrogen ferrochrome is employed as a source of nitrogen, the results are less erratic but still leave much to be desired. The addition of nitrogen by this procedure is slow, costly and falls short of the practical degree of reliability needed for the rapid and uniform production of nitrogenized products of desired alloy contents.

One of the outstanding objects of my invention is the efficient, economical and thoroughly practical production of stainless steel, either with or without supplementary additions indicated above, wherein a desired nitrogen content is rapidly and reliably achieved.

Referring more particularly to the practice of my invention, I provide in a suitable stainless steel production furnace, for example in an electric arc furnace, a meltdown charge of desired raw materials, such as stainless steel scrap and/or low-carbon steel scrap and an oxidizing agent such as iron ore, roll scale, or the like. I melt down this charge, thereby forming a bath of ferrous metal covered by an oxidizing slag, and bring the melt to a uniformly high temperature. I add chromium in the furnace either along with the initial meltdown ingredients, using, for example, high carbon ferrochrome or chrome ore, or illustratively through the addition of chrome ore to the bath and slag formed as indicated above. It usually is advantageous for such reason as savings in power consumption, improved furnace operating conditions, and the like, to introduce the chromium additions both along with the initial charge of ingredients and to the bath of metal and slag after meltdown. This is particularly true in using chrome ore as a source of chromium, for the procedure tends to alleviate crowding of the furnace and enables the successful consumption of maximum amounts of the ore.

The supernatant, strongly oxidizing slag formed on the molten metal by virtue of the meltdown, and the high temperatures employed, enable an effective exclusion and/or elimination from the

metal bath of any carbon coming from the furnace electrodes and furnace atmosphere, as well as from the raw materials melted. Along with the oxidation of carbon at these high temperatures, there is an incidental oxidation of chromium from the metal; the chromium oxides formed being transferred into the slag.

After achieving a substantially complete meltdown of the ingredients to form a ferrous metal bath of low-carbon content covered by a slag containing oxides of iron and chromium, as indicated above, I charge a suitable reducing agent, such as ferrosilicon into the furnace, for recovering iron and chromium from their oxides in the slag, thereby increasing efficiency and economy of production. I prefer to add along with the reducing agent a suitable quantity of basic slag-forming material or materials, such as burnt lime, to assure basic conditions during the reduction of oxides contained in the slag and a consequent minimum attack by acid slag constituents on the furnace lining.

The ferrosilicon or other suitable reducing agent effects the reduction of oxides of iron and chromium in the slag; thereafter the metallic values resulting from the induction gravitate from the slag into the underlying bath of metal. When the reduction continues to such extent as further recovery of iron and chromium becomes a negligible factor, I draw off the slag and prepare to finish the metal. For this purpose, I build up a finishing slag, illustratively of ferrosilicon and burnt lime, on the metal surface.

With regard to the introduction of nitrogen to melts comprising chromium and iron, I have made the highly important discovery that the presence of soluble metal oxides greatly impairs bath efficiency in absorbing nitrogen, and that a positive deoxidation treatment applied to the bath either before or during the introduction of nitrogen is conducive to rapid and highly satisfactory nitrogen pick-up by the metal. The exact reason for impaired solubility of nitrogen in oxide-containing baths is not fully understood by me. It may be that the oxides exist in solution in the form of chromium-iron-oxygen compounds, are inert, and represent a depletion of free chromium which otherwise would be highly active in absorbing nitrogen in the melt; however, I do not wish to be bound by any such explanation.

I deoxidize the metal bath for nitrogen treatment and introduce the nitrogen all preferably during the metal finishing operation and illustratively while the particular finishing slag just mentioned is on the metal surface. The deoxidizing agent which I employ illustratively is 1.5 pounds of aluminum (as contained in ferro-aluminum) per ton; based on tapping weight of the bath. I make the ferro-aluminum addition through the finishing slag by rabbling thoroughly into the melt as furnace conditions permit. This gives a rapid and substantially complete deoxidation of any oxides in the melt, leaving the metal clean and ready for treatment with nitrogen.

Either during or after the deoxidation operations, or while the deoxidation is in progress and continuing after the completion of the same, I introduce nitrogen to the melt, advantageously by bubbling a gentle flow of nitrogen gas directly through the molten metal beneath the finishing slag, as by means of an iron pipe or a suitable refractory metal tube. An efficient absorption of nitrogen by the molten metal rapidly ensues.

As illustrative of the absorption of nitrogen, the following data from comparative induction heats is given in Tables I and II below:

TABLE I

ABSORPTION OF NITROGEN BY MOLTEN STAINLESS STEELS

Identification of samples

Heat No.	Analysis of Blank		
	C	Cr	N
E2783	.027	12.30	.025
E2962	.031	12.90	.024
E3067	.109	26.25	.031
E3076	.113	26.13	.014
E3077	.119	26.07	.044

Indication of the absorption of nitrogen had by my process for a 12% chromium grade of stainless steel is illustrated by the comparative heats E2783 and E2962. While for a 26% chromium grade it is indicated by the comparative heats E3067 and E3076 and E3077. The amount of nitrogen picked up during the making of any particular heat, of course, is represented by the difference between the values given in Table II for the heat and that given in Table I.

TABLE II

Nitrogen absorption data

Heat No.	5 min. N	10 min.			15 min. N	20 min. N
		C	Cr	N		
E2783	-------	.025	12.24	.026	-------	-------
E2962	-------	.032	12.87	.100	-------	-------
E3067	.030	------	-------	.031	.037	.049
E3076	.120	------	-------	.179	.271	.292
E3077	.106	------	-------	.148	.199	.244

In my process, I find advantage in holding the melt at as low a temperature as practical during the deoxidizing and nitrogenizing period, this preferably being below 3000° F. and generally below 2950° F. At temperatures of superheat the deoxidizing ability of aluminum, for example, appears to be less than at relatively low temperatures; and the efficiency of nitrogen recovery increases with decrease in temperature to below temperatures of superheat. The optimum low temperature range, however, varies considerably with many different grades of stainless steel which I produce and thus is determined empirically in specific practice. Examples of the effect of temperature, however, are given in the Table III below:

TABLE III

ABSORPTION OF NITROGEN BY MOLTEN STAINLESS STEELS

Temperature effect

[Both heats deoxidized prior to the introduction of nitrogen]

Heat No.	Original Analysis			Temperature	After 5 min., N
	C	Cr	N		
				° F.	
E3043	.057	19.05	.027	2950	.110
E3044	.053	17.85	.027	3070	.069

In general, in accordance with my practice, I achieve a nitrogen content of approximately 0.07% to 0.30% or higher, by bubbling say 0.6

cubic feet of commercial bottled dry nitrogen per minute from a one inch silica tube for 5 to 10 minutes' time while holding the bath at about 2950° F. Commercial bottled dry nitrogen is an available and relatively inexpensive source of nitrogen gas which lends itself to an ease of operation and precise control.

As an alternative, or in conjunction with the use of commercial bottled nitrogen, I employ any other suitable nitrogen-bearing material or materials desired, as for example ammonia in latent or nascent stage, cyanamides, ferro-cyanide, copper cyanide, urea, or the like. Any additions of the decomposible solid sources of nitrogen conveniently are made through the finishing slag and by rabbling into the underlying metal.

Once the source or sources of nitrogen contact the bath, there begins a rapid, efficient and reliable absorptive action wherein the nitrogen is absorbed by the chromium-iron alloy metal. Soon, with continued treatment, as with the bubbling gas, the active metal takes up a sufficient quantity of nitrogen as desired.

Before tapping the heat I add, if desired, amounts of any such supplementary elements as nickel, copper, manganese, cobalt, columbium, titanium, molybdenum, tantalum, tungsten, vanadium or the like, in accordance with standard practice. I then pour the finished melt into suitable molds and allow the poured metal to cool. The resulting product is a clean, nitrogen-containing stainless steel of desired properties.

Thus it will be seen that there is provided in this invention an art and product in which the various objects hereinbefore noted together with many thoroughly practical advantages are successfully achieved. It will be seen that the process of producing stainless steels of a desired nitrogen content may be efficiently and economically attained with a minimum of effort and/or special equipment.

While in the embodiment of my invention, illustratively set forth above, a bath of ferrous metal containing chromium covered by a slag containing oxides of iron and chromium is prepared by melting down a charge of stainless steel scrap, chrome ore, and mill scale, it will be understood that any desired raw materials such as ordinary scrap, and/or stainless steel scrap as of straight-chromium and chromium-nickel varieties, high-carbon ferrochrome and/or chrome ore, and iron oxide and/or nickel oxide may be melted down to form a bath of metal including iron and chromium covered by a supernatant slag comprising metal oxides and these oxides reduced to effect a recovery of the metals, where such procedure is found desirable for the provision of a chromium-rich ferrous metal bath for treatment in accordance with my deoxidizing and nitrogenizing operations.

Likewise, while in the embodiment illustratively set forth above the steel is melted in the electric arc furnace, it will be understood that the ferrous metal bath of high chromium content, or high chromium and nickel contents, may be prepared in an induction furnace or even a fuel-fired furnace such as the open-hearth. In accordance with my invention, these melts are deoxidized by the addition of aluminum shot, ferro-aluminum, aluminum-silicon or other suitable agent as above. During this deoxidation, or immediately thereafter, it will be understood that I introduce nitrogen by way of commercial bottled nitrogen, or a decomposible nitride.

Although I prefer to effect my deoxidizing and nitrogenizing treatment during and as a part of the metal finishing stage, either in the furnace, or in the ladle after tapping tht melt from the furnace, or deoxidation in the furnace and nitriding in the ladle, good results also are obtained otherwise as by deoxidizing and nitrogenizing the metal after meltdown of the charge under oxidizing conditions and during the ensuing oxide slag reduction period before finishing the metal.

As many possible embodiments may be made of my invention and as many changes may be made in the embodiments hereinbefore set forth, it will be understood that all matter described herein is to be interpreted as illustrative and not in a limiting sense.

I claim:

1. In the production in an electric furnace of stainless steel containing at least 0.07% nitrogen wherein there is prepared a bath of stainless steel containing about 10% to 30% chromium and of low carbon content and having oxides of chromium dispersed therethrough, the art which comprises adding to said metal bath a deoxidizing agent of the group consisting of aluminum and calcium-silicon for substantially depleting chromium oxides and thereby increasing the ability of the metal to absorb nitrogen, and adding one of the group consisting of nitrogen gas and a decomposible nitride to said treated bath whereby there is achieved stainless steel of desired nitrogen content.

2. In the production in an electric furnace of stainless steel containing at least 0.07% nitrogen wherein there is prepared a bath of stainless steel containing about 10% to 30% chromium and of low carbon content and having oxides of chromium dispersed therethrough, the art which comprises dispersing a deoxidizing agent of the group consisting of aluminum and calcium-silicon through the metal bath for substantially depleting chromium oxides and thereby increasing the ability of the metal to absorb nitrogen, and immediately thereafter introducing nitrogen to the treated bath whereby the desired nitrogen content is achieved.

3. In the production in an electric furnace of stainless steel containing at least 0.07% nitrogen wherein there is prepared a bath of stainless steel containing about 10% to 30% chromium and of low carbon content and having oxides of chromium dispersed therethrough, the art which comprises subjecting said bath to deoxidation treatment with at least one material of the group consisting of aluminum and calcium-silicon for substantially depleting chromium oxides and thereby increasing the ability of the metal to absorb nitrogen, and during said deoxidation treatment bubbling commercial bottled dry nitrogen gas through said bath whereby there is achieved a desired nitrogen content.

4. In the production in an electric furnace of stainless steel containing at least 0.07% nitrogen wherein there is prepared a bath of stainless steel containing about 10% to 30% chromium and of low carbon content and having oxides of chromium dispersed therethrough and having a thin finishing slag thereon comprising lime and ferro-silicon, the art which comprises subjecting the bath to deoxidation treatment with aluminum for substantially depleting chromium oxides and thereby increasing the ability of the metal to absorb nitrogen, and while maintaining the bath at a temperature below 3000° F. introducing

nitrogen into said bath whereby the desired quantities of nitrogen are had.

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