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PRODUCTION OF HIGH NITROGEN MANGANESE ALLOY

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My invention, directed generally to the field of alloy metals, relates more particularly to a process for producing alloy steels of high manganese and nitrogen contents.

An object of my invention is to provide a simple and direct process for producing nitrogen-containing iron alloys of high manganese content, which method requires but little time and labor using standard furnacing equipment, readily available in the industry.

Another object is to provide a process, economically practiced, for producing nitrogen-containing high manganese stainless steels, which method, highly effective and readily employed, uses a clean and inexpensive material of high nitrogen and manganese contents readily stocked and constantly available for use in conjunction with operations now employed in steel production.

Yet another object is to provide a process for introducing both nitrogen and manganese into alloy steels, enabling the production in simple and direct manner of steels displaying high resistance to elevated temperatures.

Other objects in part will be obvious and in part pointed out hereinafter during the course of the following description.

My invention accordingly may be seen to reside in the several operational steps, and in the relation of each of the same to one or more of the others, all as described herein, and the scope of the application of which is more fully indicated in the claims at the end of this specification.

As conducive to a better understanding of certain features of my invention, it may be noted that considerable study has been directed towards the production of alloy steels suitable for resisting the high temperatures and other severe conditions encountered in internal combustion engine duty. Particular difficulties are experienced in the production of satisfactory exhaust valves because of the corrosive conditions encountered at high temperatures, this in combination with the wash and scour of hot gases and great mechanical pounding. It is not uncommon to encounter temperatures of 1400° F. and even higher in such practice; and it is mandatory that the valves employed resist corrosion at these temperatures and display requisite hardness. Present practice requires that they possess high resistance to the combustion products of the leaded fuels at the high operating temperatures prevailing. Valve steels of this general type are known in the art, typically analyzing about 21% chromium, approximately 4% nickel, about 8% manganese, and about 0.4% nitrogen, more broadly, chromium 12% to 30%, nickel 2% to 35%, manganese 3% to 12% and nitrogen .06% to .40%. The steels additionally may include 1.5% to 9% molybdenum and nitrogen up to .60%. They comprise the subject matter of certain pending patent applications of Paul Jennings, Serial Nos. 141,291 and 195,630, filed January 30, 1950 and November 14, 1950, respectively, and entitled High Temperature Articles, now U. S. Letters Patent 2,602,738 and 2,671,726 of July 8, 1952 and March 9, 1954.

Certain practical difficulties, however, are encountered in the production of the nitrogen-bearing stainless steels; and my present invention is primarily directed towards a simple and direct yet highly satisfactory method of introducing both nitrogen and manganese into the steel during the production thereof. Illustratively, known processes are highly expensive. Frequently the ingredients employed are either difficult to procure or costly to prepare, or both. In many instances they can be handled

only with substantial waste. Others contain detrimental impurities. Moreover, not infrequently difficulty is observed in controlling the amount of nitrogen absorbed by the stainless steel bath, and this because of the nature of the nitrogen-containing material. From all the foregoing, it will be seen that many important factors must be considered when introducing nitrogen into ferrous alloys.

Accordingly, an important object of my invention is to provide a simple, direct and inexpensive process for the production of stainless steel of high nitrogen and high manganese contents in which both nitrogen and manganese are in exact and proper quantities, and this without the addition of carbon or other objectionable ingredient or impurity inconsistent with the specifications of the alloy steel being produced.

And now, referring more particularly to the practice of my invention, I first prepare a bath of steel to a desired analysis of iron and other metal, with carbon content held at desired value. And following the preparation of the bath, I make up a finishing slag on the surface thereof and then add thereto a nitrogen-bearing manganese-containing metal or pre-alloy. Such a metal or pre-alloy forms the subject of my companion application Serial No. 205,603 filed of even date herewith and entitled Manganese-Nitrogen Pre-Alloy and Method. Therein I disclose that such a pre-alloy may comprise either a high nitrogen electrolytic manganese or a high nitrogen ferro-manganese. Of these pre-alloys, the electrolytic manganese contains upwards of 93% to 99% manganese and in the neighborhood of 1 or 2% up to about 7% nitrogen. While the ferro-manganese pre-alloys, of low-carbon or medium-carbon content, contain upwards of approximately 60% manganese and from 1 or 2% to about 5% nitrogen.

The addition of the nitrogen-bearing manganese pre-alloy is accomplished rapidly and in simple manner by shovelling the same onto the bath and then rabbling it into the melt. In this maner both the manganese and nitrogen are together introduced in simple and highly satisfactory manner. Moreover, while in certain known processes hitherto employed, the pick-up of the nitrogen into the stainless steel bath is no more than about 50%, I find that substantially all of the nitrogen and approximately 85% of the manganese are effectively carried into the metal, the loss of nitrogen being insignificant and that of manganese, through oxidation, amounting to about 15%. Accordingly, I find that it is necessary to employ only comparatively small quantities of the nitrogen-bearing ingredient in order to achieve good results.

And now, as illustrative of the practice of my invention, I produce a heat of stainless steel in any well-known manner, as for example, by employing stainless steel scrap and ferro-chromium of high-carbon content as disclosed, illustratively, in the Feild Patent 1,925,182; or in accordance with Arness 1,954,400, where rustless iron scrap and chromium ore are used as the principal sources of chromium; or through the use of rustless iron scrap, high-carbon ferro-chrome and chrome ore as described in Arness 2,056,162. Such steel ordinarily contains 5% to 35% chromium, with or without nickel in amounts up to 30%, and with or without any one or more of silicon, aluminum, manganese, copper, molybdenum, cobalt, tungsten, vanadium, titanium, columbium, tantalum, sulphur, phosphorus and the like in small amounts for special purposes.

The metal bath as produced according to the practice of any of the aforementioned patents, is processed through the oxidizing and reducing stages, and the slag drawn off. A finishing slag of lime and fluorspar is then prepared on the surface of the bath. It is onto this finishing slag that I preferably charge the pre-alloy, although certain benefits are had even where the pre-alloy is added during the reducing stage of the process. In both instances, however, I prefer to initially heat the pre-alloy before adding it to the bath.

Illustratively, with a bath of say 10,000 pounds of stainless steel, analyzing about 23% chromium, about 4.5% nickel, 0.6% carbon and remainder iron, both manganese and nitrogen in approximately the required amounts may be added by way of the nitrogen-bearing

metal or pre-alloy. Employing about 1100 pounds of the nitrided electrolytic manganese with an approximate 95% manganese content, and a 5.0% nitrogen content, giving a manganese-nitrogen ratio of about 19 to 1, there is achieved steel containing about 8.7% manganese (the manganese recovery amounting to about 87%), and about 0.54% nitrogen, some 0.04% nitrogen initially being present in the steel. Additionally, the steel contains about 21.2% chromium, 4.1% nickel, about 0.6% carbon and remainder iron. Thus, the required manganese-nitrogen ratio is directly produced by adding the high-nitrogen-bearing electrolytic manganese.

Where desired I also produce the high nitrogen-high manganese stainless steels with the addition of the iron-manganese pre-alloys. With an 86% low-carbon ferro-manganese, containing about 3.0% nitrogen, I find that about 1300 pounds of the same gives steel with a manganese content of about 8.8% (the manganese recovery being about 87%), and a nitrogen content of about 0.39%, this where the steel initially contains 0.03% nitrogen. Thus, I effectively produce an internal combustion engine valve steel of the manganese and nitrogen contents hereinbefore set forth, with either high-nitrogen electrolytic manganese, high-nitrogen ferro-manganese of the low-carbon or medium-carbon grades.

In the practice of my process, I add just sufficient high-nitrogen manganese-containing metal or pre-alloy as is necessary to impart the proper manganese and nitrogen contents to the bath. Upon thorough rabbling, the nitrogen is quickly assimilated throughout the metal. Apparently in these stainless steels the manganese present has an even greater thirst for nitrogen than has chromium and therefore these two alloying metals supplement each other in absorbing the available nitrogen. Substantially all of the nitrogen of the high-nitrogen manganese-containing pre-alloy, therefore, is absorbed directly by the molten bath.

Upon completion of the melt I tap the metal into a ladle, from which it is teemed into molds. Here it solidifies and cools. Upon stripping the molds, the ingots are ready for conversion into billets and bars for processing into rods or wire and then into internal combustion engine valves.

Since, in the production of high-nitrogen high-manganese stainless steel, substantially all of the pre-alloy passes directly into the metal, my process is highly effective. Because of the cheapness of the pre-alloy and the small amount required to give a desired nitrogen addition, this because of its very high nitrogen content, the process is economical as well.

Thus, it will be seen from the foregoing that I achieve a new process for the production of high-nitrogen high-manganese alloys and for introducing both nitrogen and manganese into stainless steels. By the use of my process the various objects hereinbefore noted are successfully achieved, along with many thoroughly practical advantages.

Since many possible embodiments may be made of my invention, and since many modifications may be made in the embodiments given above, I desire that all matter set forth herein be interpreted as illustrative, and not as limitative.

I claim as my invention:

1. In the production of stainless steel containing 12% to 30% chromium, up to 30% nickel, 3% to 12% manganese, .06% to .60% nitrogen, up to 9% molybdenum, and remainder substantially all iron, the art which includes preparing a bath of stainless steel containing 12% to 30% chromium, and up to 30% nickel, and adding thereto a nitrogen bearing manganese-containing metal or alloy comprising approximately 75% to 98% manganese, 2% to 5% nitrogen and the remainder iron.

2. In the production of stainless steel containing 12% to 30% chromium, 2% to 35% nickel, 3% to 12% manganese, .06% to .60% nitrogen, up to 9% molybdenum, and remainder substantially all iron, the art which includes preparing a bath of stainless steel containing 12% to 30% chromium and 2% to 35% nickel, making up on the surface of said bath a finishing slag comprising lime, and adding to the bath a pre-heated nitrogen-bearing manganese-containing alloy comprising approximately 75% to 98% manganese, 2% to 5% nitrogen and the remainder iron.

3. In the production of stainless steel containing 12% to 30% chromium, 2% to 35% nickel, 3% to 12% manganese, .06% to .60% nitrogen, up to 9% molybdenum, and remainder substantially all iron, wherein there is employed an initial melt-down period under oxidizing conditions followed by a subsequent reducing period to give a bath of steel containing 12% to 30% chromium and 2% to 35% nickel, the art which includes adding to the steel bath during the reducing period a nitrogen-bearing manganese-containing alloy comprising about 60% to 99% manganese, about 1% to 7% nitrogen and the balance iron.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,138,289	Becket	Nov. 29, 1938
2,281,179	Arness	Apr. 28, 1942

FOREIGN PATENTS

Number	Country	Date
152,291	Austria	Jan. 25, 1938

OTHER REFERENCES

Metals and Alloys, April 1944, page 859.