United States Patent Office

2,840,872

Patented July 1, 1958

2,840,872

METHOD OF ECONOMICALLY INTRODUCING ZIRCONIUM INTO STEEL

John Bidner, Youngstown, Ohio, and Phillips M. Connor, Sharon, William H. McClure, Sharpsville, and William Parks, Sharon, Pa., assignors to Sharon Steel Corporation, Sharon, Pa., a corporation of Pennsylvania

No Drawing. Application January 14, 1952
Serial No. 266,442

3 Claims. (Cl. 22—215)

The invention relates to high strength, low alloy steels containing zirconium as an alloying element and more particularly to an economical method of introducing zirconium into such steels.

High strength, low alloy steels have rather wide application in those fields where a reduction in weight may mean a considerable saving both in original cost and in operating costs. Such steels constitute a specific class in which inherent mechanical properties and resistance to atmospheric corrosion are obtained by incorporating therein small proportions of one or more alloying elements other than carbon. Such steels are normally used, as rolled, as annealed, as normalized or as stress relieved, without further heat treatment since their physical properties are inherent in the "as rolled" condition. These steels have unusual ductility, high resistance to impact and fatigue, excellent welding characteristics, resistance to abrasion, etc.

There are a number of compositions which, when the alloying element percentages are critically maintained, provide the characteristics desired in a high strength, low alloy steel. Among these compositions are some which include zirconium as an element.

Such steels are ordinarily purchased by a user on the basis of a guaranteed analysis or chemical specification because, unless the specifications are critically maintained, the steel does not have the properties or characteristic intended.

It has been exceedingly difficult in the manufacture of high strength, low alloy steels containing zirconium, to obtain the required amount of zirconium in the steel produced in an economical manner.

Zirconium has long been used in the manufacture of steel as a degasifying or deoxidizing or scavenging agent by using ladle or mold addition agents containing zirconium and other elements or metals either mixed or alloyed. However, it also long has been known that a large proportion of the zirconium present in the addition agent is consumed when added to steel in the manufacture thereof in accordance with prior practice, and no zirconium or only a small amount thereof remains in the final alloy produced. Information in this connection is set forth in Patents Nos. 1,503,772, 1,614,920, 1,959,399 and 2,546,525.

These problems, difficulties and conditions have rendered the manufacture of high strength, low alloy steels containing zirconium excessively expensive because of the large amounts of very expensive zirconium which are lost or consumed in providing the guaranteed percentage of zirconium in the steel produced.

Typical analyses of zirconium-containing high strength, low alloy steels are set forth in Patents Nos. 2,234,130, Re. 22,072, 2,416,648 and 2,416,649. More specifically, zirconium-containing high strength, low alloy steels may contain, in addition to iron, the following elements intended in the steel produced in practice to be within the following specified ranges:

	Percent
Carbon	.10–.14
Manganese	.60–.80
Silicon	.70–.90
Chromium	.50–.65
Zirconium	.05–.11
Sulphur	.03–max.
Phosphorus	.03–max.

Another percentage range of elements providing a high strength, low alloy zirconium-containing steel is as follows:

	Percent
Carbon	.10–.20
Manganese	.40–.60
Silicon	.50–.75
Chromium	.35–.55
Zirconium	.03–.08
Sulphur	.03–max.
Phosphorus	.03–max.

Specifically, in the commercial manufacture of high strength, low alloy steels meeting the foregoing specifications, we have encountered in the steel produced only about a 15% yield or recovery of the amount of zirconium originally introduced into the heat and sometimes all of the zirconium is lost. Various expedients to obtain a better yield of zirconium in the steel produced were tried. The time, place, manner and form of making zirconium additions were varied without any substantial increase in the zirconium yield.

We found in the course of investigation, by trial and error, that the zirconium yield in the steel produced could be slightly increased to about a 23% recovery by making the zirconium addition to the mold rather than to the ladle, but this practice did not provide an appreciable saving in the expensive zirconium losses.

Then we discovered that by adding zirconium mixed with a small amount of aluminum in the form of aluminum shot to an ingot mold as the molten metal is being poured therein, an average of an 85% yield of zirconium in the steel produced can be obtained.

Further investigation disclosed that a high yield of zirconium cannot be obtained if the aluminum is omitted or if the aluminum is placed in the bottom of the mold prior to pouring and the zirconium is fed to the mold during pouring.

Accordingly, it is an object of the present invention to provide a novel method of introducing zirconium economically into steel.

Furthermore, it is an object of the present invention to provide a new method of substantially reducing the cost of manufacturing zirconium-containing high strength, low alloy steels.

Moreover, it is an object of the present invention to substantially reduce the consumption of zirconium in manufacturing steel required to have a guaranteed amount of zirconium therein within fixed limits.

Likewise, it is an object of the present invention to provide a new method of introducing zirconium into steel by which the amount of zirconium present in the steel produced can be predicted, thereby avoiding the production of rejectable material which does not satisfy specifications as to zirconium content.

Furthermore, it is an object of the present invention to avoid developing undesirable characteristics or properties in a zirconium-containing high strength, low alloy steel incident to the control of the manner of introducing zirconium therein in an economical manner.

Finally, it is an object of the present to overcome the described difficulties heretofore encountered in the manufacture of zirconium-containing steel, and to obtain the

described objectives, benefits and new results in an inexpensive and easily controlled manner.

These and other objects and advantages apparent to those skilled in the art from the following description and claims may be obtained, the stated results achieved, and the described difficulties overcome by the methods, steps, operations and procedures which comprise the present invention, the nature of which is set forth in the following general statement, a preferred embodiment of which—illustrative of the best mode in which applicants have contemplated applying the principles—is set forth in the following description, and which are particularly and distinctly pointed out and set forth in the appended claims forming part hereof.

The nature of the discoveries and improvements of the present invention in a method of introducing zirconium into steel to obtain a high zirconium yield in the steel produced may be stated in general terms as including the steps of providing fully killed steel in a ladle, pouring the fully killed steel into an ingot mold, and feeding zirconium mixed with aluminum into the mold as the steel is being poured.

The method of the present invention will be described with reference to the actual commercial manufacture of zirconium-containing high strength, low alloy steel.

In accordance with the present invention, a heat of steel is made in the usual manner, the desired carbon content obtained, and the alloying elements such as manganese, chromium and silicon added in accordance with usual practice for making killed steel. The steel of the heat collected in one or more ladles thus has the desired analysis except for zirconium content and perhaps an incomplete amount of silicon to satisfy the silicon content requirement. The molten metal is then ready to be poured from the ladle into ingot molds.

A trough or chute is provided for each ingot mold as the same is being poured. The required quantity of zirconium or zirconium-containing alloy is placed in the trough or chute and a small amount of aluminum in the form of aluminum shot is disbursed across the top of the zirconium in the trough. As the ingot mold is being poured, the zirconium and aluminum addition is fed to the mold from the beginning of pouring so that all of the zirconium addition is fed to the mold by the time that the mold is filled to approximately one foot from the top thereof.

Check analyses of the metal in the ingot taken from various sections of the ingot disclose a substantially uniform zirconium analysis throughout the ingot with approximately an 85% recovery in the ingot of the amount of zirconium introduced into the mold while pouring.

The normal practice for introducing zirconium into steel is to add the same in the form of zirconium-silicon-iron alloy containing from 35% to 45% zirconium, approximately 49% silicon and the balance iron. Thus, the silicon in the zirconium alloy addition completes the amount of silicon necessary to satisfy the silicon content requirement.

In accordance with the present invention, this 35–45% zirconium alloy addition is used as a mold addition at the rate of about 16 to 20 pounds of the zirconium-silicon-iron alloy plus one pound of aluminum shot, to each mold where a high zirconium content of .05–.11% is desired in the steel produced. Where a .03–.08% zirconium content is specified, the mold addition may constitute approximately 10 pounds of zirconium-silicon-iron alloy per mold plus one pound of aluminum shot.

Authorities in the field of high strength, low alloy steel caution against the use of aluminum after the steel has been killed, in the production of the desired analysis, because it is believed that the presence of aluminum is a detriment to obtaining the desired properties in the high strength, low alloy steel and particularly in the welding characteristics thereof. However, we have discovered that the small amount of aluminum used mixed with the zirconium in the mold addition as described does not produce any detrimental qualities, characteristics or properties in the steel produced; and in fact, the usual analysis of the steel produced does not disclose the presence of aluminum therein.

We present below in Table I a record of a series of heats of high strength, low alloy steel made in accordance with the present invention, listing the pounds of zirconium used for each heat, the amount of zirconium present in the steel determined by analysis, and the pounds of zirconium used per percentage point of zirconium in the steel produced.

Table I

Heat No.	Lbs. Zirc. Used	Percent Zirc.	Lbs. Zirc./ Percent Point
A	525	.06	88
B	496	.07	71
C	496	.07	71
D	500	.06	83
E	500	.06	83
F	500	.07	71
G	500	.06	83
H	500	.06	83
I	512	.05	102
J	480	.06	80
K	496	.06	83
L	320	.03	107

Taking an average of the figures in Table I, in accordance with the present invention, an average of 84 pounds of zirconium is required for each percentage point of zirconium in the steel produced; and a relatively high percentage of zirconium can be definitely predicted to be present in the steel produced, with the use of only a little more than the calculated amount of zirconium necessary because of the high 85% yield obtained.

These results may be compared with the results obtained in accordance with prior practice as shown in Table II.

Table II

Heat No.	Lbs. Zirc. Used	Percent Zirc.	Lbs. Zirc./ Percent Point
1	1,500	.07	214
2	700	.01	700
3	1,200	.01	1,200
4	1,500	.09	167
5	1,500	.02	750
6	930	.02	465
7	460	.01	460
8	815	.02	408
9	850	.03	283
10	815	.03	272
11	773	.01	773
12	928	.01	928
13	900	.02	450
14	820	.03	273

In Table II, an average of 524 pounds of zirconium is required for each percentage point of zirconium contained in the steel produced, and at the same time the results are very unpredictable, as is disclosed by a comparison of heats Nos. 4 and 5 wherein the same amount of zirconium was used while the resulting analysis was .09% zirconium for heat 4 and .02% zirconium for heat 5. Similarly, only .01% zirconium was obtained in each of heats 3 and 7 which require 1200 pounds of zirconium for heat 3 and only 460 pounds of zirconium for heat 7.

Although we have not arrived at an exact explanation as to why the exceptional results of the present invention are obtained, it is possible that when a zirconium addition is made to a ladle at the same time that the manganese, silicon and aluminum additions are made, because the ladle may contain as much as 135 tons of steel, and the silicon, aluminum and zirconium additions may comprise as much as 4 tons of material, there may

not be sufficient time for all of the added elements to go into solution and the cooling effect of the bulk thereof may further retard the addition elements from going into solution so that the zirconium addition may act as a deoxidizer until the metal is poured, with a consequent loss of the major portion or all of the zirconium.

On the other hand, if the steel is fully deoxidized in the ladle then there is nothing left to oxidize the zirconium if the latter is added to the mold while the mold is being poured, in accordance with the present invention. Furthermore, the presence of the small amount of aluminum may create an exothermic reaction which hastens putting the zirconium into the solution.

Also, it is possible that while the stream of molten metal is pouring from the ladle into the mold, a slight amount of oxygen may be entrained by the surface portions of the falling stream of molten metal; and if this is the case, possibly this oxygen is removed by deoxidation by the aluminum mixed with the zirconium addition as it is being added to the mold.

Whatever may be the correct explanation of why the present invention provides the exceptional and outstanding new results described, nevertheless the fact remains that by the use of the invention in actual practice the yield of zirconium contained in the steel produced as compared with the zirconium added to the steel is increased from approximately 15% in accordance with prior practice to approximately 85% thereby reducing the cost and consumption of zirconium by equivalent amounts.

Accordingly, the present invention provides outstanding new results in connection with the manufacture of zirconium-containing steels and accomplishes the objectives of the present invention in a very simple manner which is easy to carry out in connection with the normal procedure for steel manufacture; and overcomes prior art difficulties and solves long standing problems in the art.

In the foregoing description certain terms have been used for brevity, clearness and understanding; but no unnecessary limitations are to be implied therefrom beyond the requirements of the prior art, because such terms are utilized for descriptive purposes herein and not for the purpose of limitation and are intended to be broadly construed.

Moreover, the description of the improvements is by way of example and the scope of the present invention is not limited to the exact details illustrated and described.

Having now described the features, discoveries and

principles of the invention, the operation and procedure of preferred method steps thereof, and the advantageous new and useful results obtained thereby; the new and useful methods, steps, operations, procedures, discoveries and principles, and mechanical equivalents obvious to those skilled in the art, are set forth in the appended claims.

We claim:

1. The method of economically introducing zirconium into steel including the steps of collecting a heat of fully killed steel in a ladle, pouring the killed steel into an ingot mold, and feeding a mixture of zirconium-containing material and aluminum in the ratio of 10 to 20 zirconium-containing material to 1 of aluminum by weight to the mold during pouring.

2. The method of obtaining an approximately 85% yield of zirconium in introducing zirconium into a high strength low alloy steel including the steps of providing a molten bath of fully killed low alloy steel in a ladle having the desired alloying elements therein except zirconium, pouring such killed steel into an ingot mold, and adding a composition of zirconium-containing alloy and aluminum to the ingot mold during pouring, the composition containing a ratio by weight of zirconium-containing material to aluminum in excess of 10 to 1.

3. The method of making zirconium-containing high strength low alloy steel including the steps of providing a bath of fully killed low alloy steel having the desired alloying elements therein except zirconium, providing a quantity of zirconium-containing material adjacent a mold, dispersing a small amount of aluminum shot on the zirconium-containing material, pouring the killed steel into the mold, and feeding the zirconium-containing material and aluminum to the mold from the beginning of pouring until the mold is filled to approximately one foot from the top thereof.

References Cited in the file of this patent

UNITED STATES PATENTS

1,374,038	Sicard	Apr. 5, 1921
1,420,328	McConnell	June 20, 1922
2,233,726	Belding	Mar. 4, 1941

OTHER REFERENCES

Transactions, American Society for Metals, vol. 28, pages 608 and 609, published in 1940 by the A. S. M., Cleveland, Ohio.

Titanium and Its Use in Steel, page 76, published in 1940 by the Titanium Alloy Manufacturing Co., Niagara Falls, N. Y.