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HIGH-CARBON RIMMED STEEL AND METHOD OF MAKING IT

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This invention relates generally to steel manufacture and, in particular to rimmed steel with a high carbon content and a method of making it.

Rimmed steel has peculiar, well known advantages for certain uses. It has been possible heretofore, however, to make rimmed steel having only a medium or low content of carbon, the maximum carbon content being .28 or .30% ("The Making, Shaping and Treating of Steel," 6th ed., p. 573). In certain applications where rimmed steel is desirable, a higher carbon content would be advantageous and it is accordingly the object of my invention to produce such steel and provide a method for making such steel. A further object is to produce ingots relatively free of pipe without the use of hot tops. A still further object is to produce high-carbon steel having good surface qualities, controlled segregation and freedom from refractory inclusions.

My invention is applicable particularly to the production of steels having a carbon content of over .35% and up to 1.10%. Briefly stated, the invention comprises adding to such steel, when it has been teemed into molds and while it is still liquid, an exothermic rimming agent of novel composition. Preferably the rimming agent is added to each mold while steel is being teemed thereinto and, specifically, before the mold is half filled. The rimming agent is composed of iron oxide and sodium fluoride, but includes also an exothermic-reaction mixture of granular aluminum and a compound affording a source of oxygen for combination therewith, such as sodium nitrate. The amount of the rimming agent used is from one to four pounds per ton of ingot weight. The following ranges are satisfactory for the several ingredients of the rimming agent:

Table I

| | Percent by weight |
|-------------------|-------------------|
| Iron oxide | 40-80 |
| Granular aluminum | 2.5-17 |
| Sodium nitrate | 5-34 |
| Sodium fluoride | 5-20 |

The amount of sodium nitrate should be double the amount of aluminum. The ingredients should be in such a state of subdivision as to pass through an 8-mesh screen and should be thoroughly mixed before use.

The iron oxide acts to promote rimming action in the liquid steel by furnishing oxygen for combination with some of the carbon present therein. The sodium nitrate furnishes oxygen for combination with the aluminum. This reaction results in the evolution of a large amount of heat serving to fuse the iron oxide and sodium fluoride without causing localized cooling of the ingot. The sodium fluoride acts as a flux to sweep upward the alumina resulting from the oxidation of the aluminum. The overall result of the addition of the rimming agent, therefore, is to put fused iron oxide and sodium fluoride into the liquid steel as it is being teemed into the mold so that, on standing thereafter, rimming will proceed vigorously for such period as necessary to form a case of the desired thickness. After the iron

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oxide of the rimming agent has reacted, a sodium-aluminate scum remains which acts as a flux and scavenger for any refractory inclusions such as silicates.

As a typical example of the practice of the invention, I make a heat of steel by conventional basic open-hearth practice except that I do not add any deoxidizer such as ferrosilicon, aluminum or ferrotitanium and magnesium, either to the bath in the furnace or to the ladle after tapping the furnace. The carbon content of the heat is brought down progressively in the furnace to approximately the desired final value, e. g., 0.65%, and ferromanganese is added as required in the furnace or in the ladle. This may be as little as a half pound per ton in one case and as much as 25 pounds per ton in another. After tapping, the steel is teemed into big-end-down, bottle-top ingot molds, i. e., without hot tops, with the addition of about 2.5 pounds per ton of ingot weight, of a rimming agent composed of 68% globular iron oxide in the form of deseamer dust, 17% sodium fluoride, 10% sodium nitrate and 5% granular aluminum. After a predetermined time for rimming, depending on the thickness of case desired, i. e., from 15 seconds to 5 minutes, the rimming action is substantially arrested by chemically "precapping," viz., the addition of about 2 oz. per ton of ingot weight, of a suitable deoxidizer such as aluminum or calcium-silicon alloy, after which the molds are mechanically capped.

One example of steel made in accordance with the invention gave the following analyses:

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Table II

| | Percent C | Percent Mn | Percent P | Percent S | Percent Si | Percent Al |
|---|-----------|------------|-----------|-----------|------------|------------|
| Ladle analysis | .67 | .22 | .015 | .024 | .02 | — |
| Recheck analysis of billets: | | | | | | |
| Entire cross section— | | | | | | |
| Top of ingot | .66 | .20 | .015 | .025 | .01 | .006 |
| Bottom of ingot | .62 | .19 | | | | |
| Surface of billet—Top of ingot | .45 | .20 | .010 | .015 | | |
| $\frac{3}{8}$ " center drillings on 2" x 2" billet—Top of ingot | .95 | .23 | .019 | .069 | .01 | .006 |

Other examples of the composition of the rimming agent are:

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Table III

| No. | Percent deseamer dust | Percent NaF | Percent Al | Percent NaNO ₃ |
|-----|-----------------------|-------------|------------|---------------------------|
| 1. | 74 | 17 | 3 | 6 |
| 2. | 71 | 20 | 3 | 6 |
| 3. | 65 | 5 | 10 | 20 |
| 4. | 53 | 17 | 10 | 20 |
| 5. | 60 | 10 | 10 | 20 |
| 6. | 41 | 17 | 14 | 28 |
| 7. | 40 | 9 | 17 | 34 |

The cross-section of ingots of high-carbon steel produced according to my invention is characterized by an outer zone or rim area of a predetermined thickness, and this area persists in the billets rolled from the ingots. In this area, the carbon and sulphur contents are approximately two-thirds of the average concentration (ladle analysis) and there is an almost complete freedom from inclusions, giving the steel exceptionally good drawing properties. The carbon and sulphur contents at the center of the cross-section are 1.5 or more times the average concentration.

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Segregation in the ingots is well controlled and may easily be kept below the limits established for many applications. The case or rim is cleaner and freer of inclusions than normal killed steel and this condition persists even at the top center of the ingots. The carbon gradient from surface to center gives desirable hardening properties. The steel when rolled into wire rod draws well into fine wire and is also easy to cold-roll into strip. The absence of silicon and aluminum and freedom from inclusions improve the electrical conductivity, making the steel particularly desirable for the production of the high-strength wire used in communication lines.

Although I have disclosed herein the preferred practice and embodiment of my invention, I intend to cover as well any change or modification therein which may be made without departing from the spirit and scope of the invention.

I claim:

1. In a method of producing steel, the steps consisting in making a heat of steel containing over .35% carbon, teeming the steel while liquid into ingot molds and, not substantially later than the early part of teeming each mold, adding to the steel contained therein from one to four pounds per ton of the ultimate weight of the ingot, of a mixture consisting essentially of from 40 to 80% iron oxide, from 5 to 20% sodium fluoride, from 2.5 to 17% granular aluminum and from 5 to 35% sodium nitrate, and then when teeming is completed, permitting rimming of the steel to proceed unchecked for a predetermined time.

2. In a method as defined in claim 1, characterized by said mixture consisting essentially of about 68% iron oxide, about 17% sodium fluoride, about 10% sodium nitrate and about 5% aluminum.

3. In a method as defined in claim 1, characterized by chemically precapping the ingot after said predetermined rimming time.

4. In a method as defined in claim 1 characterized by finally capping the molds mechanically.

5. An exothermic reaction mixture effective to produce rimming of high-carbon steel, consisting essentially of from 40 to 80% iron oxide, from 5 to 20% sodium fluoride, from 2.5 to 17% granular aluminum and from 5 to 35% sodium nitrate.

6. As an article of manufacture, a rolled billet of ductile rimmed open-hearth steel containing from .35 to 1.10% carbon, having an outer case substantially free from inclusions, the carbon content of said case being approximately two-thirds of the average carbon content of the billet as a whole, and the carbon content adjacent the center line of the billet being about 1.5 times said average.

7. As an article of manufacture, a rolled billet of steel adapted to be further hot-rolled, containing from .35 to 1.10% carbon and having an outer case substantially free from inclusions, the carbon content of said case being approximately two-thirds of the average carbon content of the billet as a whole and the carbon content of the billet adjacent its longitudinal axis being greater than said average.

References Cited in the file of this patent

UNITED STATES PATENTS

30 1,777,975 Klepsch ----- Oct. 7, 1930

OTHER REFERENCES

35 American Society for Metals, vol. 37, 1946, pp. 54-69, incl.