

[54] **METHOD OF DEOXIDIZING AND DESULFURIZING FERROUS ALLOY WITH RARE EARTH ADDITIONS**

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[57]

ABSTRACT

A procedure for improving the through thickness properties of coarse grain ferrous alloy plate through a controlled deoxidizing and desulfurizing practice. Said practice includes adding rare earth additions to the tapping stream or ladle during tapping of the unkilld or non-deoxidized molten ferrous alloy. The ferrous alloy, when processed into plates, is characterized by a low sulfur content below about .015 percent, by weight, preferably less than about .010 percent, and by excellent ductility when tensile tested in any axial direction.

7 Claims, No Drawings

METHOD OF DEOXIDIZING AND DESULFURIZING FERROUS ALLOY WITH RARE EARTH ADDITIONS

BACKGROUND OF THE INVENTION

This invention is directed to a method for improving the through thickness properties of coarse grain ferrous alloy plate, or ferrous alloy plate made according to a coarse grain practice. More specifically the invention is directed to the steel making aspects thereof, as it is concerned with the means for controlling the deoxidation and desulfurization of the said alloy through the use rare earth additions.

The processed steels of the present invention are to be distinguished from those made according to a fine grain practice. As rolled, the former are characterized by an ASTM grain size No. 1-5, whereas the latter have a grain size varying between ASTM No. 6-8.

Thus, while the crystallographic differences between fine and coarse grain ferrous plate are obvious by virtue of this description or grain size characterization, the practice to achieve said products may be less clear. Very briefly, the type of deoxidation agent selected has a strong influence on determining the grain size. For example, if a deoxidation agent such as aluminum or titanium is chosen, i.e., one that forms a precipitate, it has been observed that the formation of a precipitate around the grain boundaries prevented grain growth. Thus, a fine grain steel results. Such a steel would be chosen where strength and formability are of primary concern.

However, to satisfy different concerns, namely improved creep properties and hardenability, coarse grain steel was developed. Here, deoxidation agents like silicon were employed since they form no precipitates to prevent grain growth.

With this background, consideration may now be given to the problem of immediate concern, namely, directionality of mechanical properties. During the metallurgical examination of hot reduced ferrous alloy plates, melted according to conventional coarse grain steelmaking practices, the lack of good through thickness properties was attributed to the formation therein of large plastic silicate inclusions, causing said steel to lack ductility when tested in the through thickness direction. When such plates of coarse grain practice steel were welded into restrained structures, welding stresses were set up causing internal ruptures along planes parallel to the plate surface. These large silicate inclusions provided both numerous sites to initiate such failure and provided planes of weakness for crack propagation.

A similar problem has been observed in fine grain practice steel. As reported in Metallurgical Transactions, December 1970, in rolled aluminum-killed steels, directionality results mainly from the presence therein of elongated manganese sulfide inclusions. It was demonstrated that the problem of directionality could be reduced by the use of additives which affect the shape of the sulfides. For example, one of the additives, the rare earth metals, when added to the aluminum killed steel changed the shape of the sulfide inclusions from elongated to globular by chemical means. With sufficient additions of the sulfide modifier, the elongated manganese sulfides were completely replaced by the globular sulfides, resulting in a steel having improved

toughness and formability in the direction transverse to the rolling direction.

With the present invention, the improved properties are achieved by significantly reducing the sulfur content of the ferrous alloy through the formation of hard rare earth sulfides rather than soft deformable manganese sulfides, and by the lowering of the oxygen content. As a consequence of the latter feature, very few soft deformable silicates are formed during solidification. For reasons to be detailed hereinafter, these objectives are achieved through a controlled sequence of additives made to the steel during the tapping thereof.

SUMMARY OF THE INVENTION

A process for improving the through thickness properties of coarse grain ferrous alloy plate, comprising the steps of preparing a molten metal bath consisting essentially of, by weight, about .05 to .30 percent carbon, about .05 to .30 percent manganese, a maximum of .035 percent phosphorus, a maximum of .020 percent sulfur, balance substantially iron; and, prior to any deoxidation thereof, adding a rare earth metal in an amount of approximately 3 to 5 lbs./ton of molten metal to said molten metal to significantly reduce the sulfur and oxygen content thereof. Concurrent with the rare earth metal additions, other alloying additions, such as carbon and manganese may be made to result in a final carbon content up to a maximum of .30 percent, and up to a maximum of 1.20 percent for the manganese. Following the desulfurization and deoxidation reactions, the molten metal is cast, solidified and processed to plate thicknesses, to exhibit a final chemistry, by weight, carbon between about .05 to .30 percent, manganese between about .40 to 1.20 percent, sulfur less than about .015 percent, preferably less than about .010 percent, with the balance substantially iron, while exhibiting excellent ductility when tensile tested in any axial direction.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

In the preferred method of this invention a deoxidizing practice is taught wherein a molten ferrous alloy results having a sulfur content by weight, below about .015 percent, preferably below about .010 percent. When processed into plates, said ferrous alloy exhibits improved through thickness properties.

Until recent years the problem of directionality of mechanical properties were noted, particularly with A1-killed steels but remained unresolved. With the recognition that the problem was related to the formation herein of elongated manganese sulfide inclusions, a solution was found, namely, sulfide shape control. That is, the sulfide inclusions were changed from elongated to globular. This was accomplished by the addition of a shape control agent such as the rare earth metals, which as a sulfide are more stable than manganese sulfide and not as readily deformable at hot rolling temperatures. However, here as well as with other additions, the approach was to control rather than reduce the effect of the sulfide inclusion.

The present invention represents a departure from the prior art as it deals with the peculiarities of coarse grain steel and is not concerned with the retention of a great amount of the rare earth metal. This will be explained in greater detail hereinafter.

In the preparation of the ferrous alloys to which this invention relates, a molten metal bath consisting essentially of, by weight, about .05 to .30 percent carbon, about .05 to .30 percent manganese, a maximum of about .035 percent phosphorous, a maximum of about .020 percent sulfur, balance essentially iron, is suitably melted in a furnace. Due to the refining action of oxygen on the molten metal bath, the carbon therein is lowered while the oxygen content is raised.

The use or combustion of oxygen by the molten metal bath also serves to raise the temperature thereof. On the other hand, if desirable, scrap and/or ore may be added to the molten metal bath to counteract or lower an excessive bath temperature. In any event, by said means a desirable tapping temperature may be achieved. For optimum results, the tapping temperature should be such as to assure at least 20° to 30° F. of super heat in the teeming stream. Said super heat assures better activity with the rare earth addition. The preferred tap temperature for the ferrous alloys herein is about 2,900° F.

As indicated previously, and as known by steelmaking practitioners, the carbon content is typically lowered below the final desired level. For example, for a steel desired to have a final analysis of between about .21 to .25 percent, by weight, carbon, a typical tapping range of about .10 to .19 percent is selected. However, a higher tap carbon is not undesirable as, to be explained hereinafter, it represents a savings in the amount of rare earth additions needed to achieve the results herein. In any event, on the basis of, for instance, said tap carbon schedule, an appropriate addition of a rare earth metal or alloy, such as a rare earth silicide, is added to the tapping stream of the molten metal, or to the ladle during tapping. Since, by the nature of the melting practice, lower carbon levels signify higher levels of oxygen in the molten metal bath, there is an inverse relationship between the carbon level and the quantity of rare earth addition made to the bath. For example, with a tapping carbon range of .10 to .19 percent by weight, the quantity of rare earth metal would vary between about 5 to 3 lbs./ton of molten metal. As a 30-35 percent rare earth silicide, the total addition may vary between about 15 to about 9 lbs./ton.

The addition of the rare earth silicide to the non-killed molten ferrous alloy substantially reduces the sulfur and oxygen content thereof, and in so doing is lost to the slag. That which is retained forms hard rare earth sulfides rather than soft deformable manganese sulfides. Further, the oxygen content is lowered to such a level that very few soft deformable silicates are formed during solidification. This synergistic effect achieved by the use of a rare earth silicide to deoxidize and desulfurize a coarse grain steel results in the improved properties herein. However, if too much rare earth metal is added to the steel, it may be fine grained, as tested in accordance with ASTM Method E112. Accordingly, the deoxidation practice must be carefully balanced depending upon the tap carbon and final desired carbon content.

At this juncture, it may be helpful to summarize several exemplary processes utilizing the invention herein. In each said process the additions to the 220 ton B.O.F. heats during tapping were made in the following sequence:

a. coal, if carbon content had to be raised,

- b. a portion, typically about 1/2, of the total manganese addition,
- c. rare earth addition to deoxidize and desulfurize,
- d. remaining manganese addition to raise final content to desired level,
- e. ferrosilicon,
- f. burnt lime.

The summary thereof is reported in Table I below.

TABLE I

Chemistry and Furnace Data	Heats				
	1	2	3	4	5
Preliminary Chemistry					
tap carbon, wt. %	.24	.12	.20	.17	.15
residual manganese, wt. %	.19	.10	.16	.15	.12
tap sulfur, wt. %	.009	.010	.008	.007	.014
Tapping Data					
tap temperature, °F.	2870	2900	2895	2890	2915
elapsed time, min.	4	5	8	4	4
Ladle Additions (lbs.)					
Coal		350		200	150
Ferromanganese		3700	2400	3500	2600
Low carbon ferromanganese	3100		1000		
Rare earth silicide	2200	3080	2200	2640	2640
Ferrosilicon	1210	550	1210	880	880
Burnt Lime	1200	1210	1200	1200	1200
Final Chemistry					
Carbon, wt. %	.24	.22	.23	.24	.20
Manganese, wt. %	.67	.69	.72	.68	.50
Phosphorus, wt. %	.009	.007	.010	.008	.011
Sulfur, wt. %	.005	.004	.005	.005	.009
Silicon, wt. %	.25	.26	.27	.23	.21
Cerium, wt. %*	.015	.020	.012	.022	.012
Iron	Bal.	Bal.	Bal.	Bal.	Bal.

* analysis of other rare earth metals not determined, but typically the total rare earth metal content is approximately twice the cerium content.

After processing from ingots into plates, each plate was tested for elongation and reduction of area. Average results along with grain size, are reported in Table II.

TABLE II

Heat	ASTM G.S.	Thru Thickness	
		Elongation	R. A.
1	1-4	22.0%	29.1%
2	3-5	32.7%	41.9%
3	1-4	20.1%	27.9%
4	1-5	28.1%	39.2%
5	1-4	29.0%	40.7%

The significance of these results may be seen from a comparison with similar steels produced according to a coarse grain practice, but without deoxidation and desulfurization in the manner taught herein. For five heats of ASTM Grade A-515, the averages for 32 tests were 12.2 percent Elongation and 12.4 percent Reduction of Area. Thus, by the procedure of adding rare earth additives to an oxygen laden unkill steel, it is possible to significantly lower the sulfur and improve the through thickness properties while maintaining a coarse grain size A.S.T.M. No. 1-5.

We claim:

1. A process for improving through thickness properties of coarse grain ferrous alloys processed into plates, characterized by the steps of preparing a molten metal bath of a non-deoxidized ferrous alloy consisting essentially of, by weight, about .05 to .30% carbon, about .05

to .30% manganese, up to about .020% sulfur, with the balance substantially iron, maintaining said molten metal bath at a temperature sufficient to insure at least 20° F. of super heat, deoxidizing and desulfurizing said ferrous alloy by the addition thereto of a rare earth metal in an amount between about 3 to 5 lbs./ton of molten metal, further modifying the chemistry of the ferrous alloy by the addition of carbon, manganese and silicon so as to produce a final chemical analysis having a maximum of about .30% carbon, a maximum of about 1.20% manganese, a maximum of about .35% silicon a maximum of about .015% sulfur, balance substantially iron, solidifying said deoxidized and desulfurized ferrous alloy and processing it into plates, where said plates are characterized by improving through thickness properties and a grain size between about ASTM No. 1-5.

2. The process according to claim 1 wherein said molten metal bath is prepared in a furnace and that said additions are made to the molten ferrous alloy as it is transferred therefrom.

3. The process according to claim 1 wherein said rare earth metal is added as a 30-35 percent rare earth silicide in an amount of between 9 to 15 lbs./ton of molten

metal.

4. The process according to claim 1 wherein said maximum final sulfur content is less than about .010 percent.

5. The process according to claim 3 where there is an inverse relationship between the carbon content of the molten metal bath and the amount of rare earth silicide added thereto, including the step of making a preliminary determination of the carbon content of the said bath and adding only that amount of rare earth silicide needed to effect the desired deoxidation and desulfurization.

6. The process according to claim 2 wherein said molten ferrous alloy is transferred from said furnace at a temperature of about 2,900° F.

7. The process according to claim 2 wherein the initial carbon content is between about .10 to .19 percent, and that said additions are made in the following sequence: coal, a portion of the manganese addition, rare earth, balance of the manganese needed to achieve the predetermined final content, ferrosilicon and burnt lime.

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